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10 Research and Development Technical Report

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INVESTIGATION OF THE ENVIRONMENTAL CONSEQUENCES OF DISPOSAL OF THE LITHIUM ORGANIC-ELECTROLYTE/SO₂ BATTERY

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K. Crumrine
E. Juergens
C. Colburn
M. Slimak
J. Freed
L. McCandless
VERSAR, INC.
6621 Electronic Drive
Springfield, VA 22151

DAAB#7-76-C-1752

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from discharged standard composition cells. Disposal recommendations for the standard cell include secured landfills or disposal ponds. Laboratory analysis of solubility tests showed an average of 0.16 mg of cyanide per cell in the discharged modified composition cell. Disposal recommendations for the modified cell are sanitary landfills or the equivalent.

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INVESTIGATION OF THE ENVIRONMENTAL CONSEQUENCES
OF DISPOSAL OF THE LITHIUM ORGANIC-
ELECTROLYTE/SO₂ BATTERY

I. INTRODUCTION AND SUMMARY

The lithium organic-electrolyte/SO₂ battery is a new primary battery which has many advantages over existing primary batteries. The superior electrical properties of the battery are produced by an electrochemical system which contains some unconventional materials and uses a non-aqueous electrolyte. The major components of the battery system investigated include lithium metal as the anode, a carbon cathode consisting of a mixture of carbon and teflon on a support screen, and an electrolyte consisting of lithium bromide and sulfur dioxide dissolved in acetonitrile (propylene carbonate may be mixed with the solvent). Conventional materials are used for separators inside the battery and for the outside jacket.

Because of the potential hazardous or toxic nature of some of the battery components, the U.S. Army contracted with Versar, Inc. for a study on the environmental consequences of the disposal of the battery. The objective of this program is to provide recommendations for low cost environmentally acceptable disposal procedures for both large and small quantities of the battery.

This program was conducted in two phases. The first phase was conducted between September 1976 and March 1977, while the second phase was started in July 1977 and ended in January 1978. The results of the first phase were described in detail in an interim report published in July 1977 as Research and Development Technical Report ECOM-76-1752-1. The Phase I Interim Report contains the following detailed types of information:

- A collection of available toxicity data and an evaluation of the relative hazardousness of the battery components as they exist in the cell, plus the by-products which could be produced in a landfill leachate;

- A compilation and description of standard disposal practices for potentially hazardous wastes;
- A listing of state and federal regulations concerning disposal of potentially hazardous wastes;
- Results of laboratory analysis for cell components and by-products in an aqueous solution, made by cutting open charged and discharged cells and immersing them in distilled water;
- Results of laboratory analysis for adsorption of cell constituents and by-products in an aqueous solution containing different types of soil; and
- Results of laboratory analysis for cell constituents and by-products in the leachate from a soil column containing sandy loam type soil.

The most significant result obtained in the Phase I study was that cyanide was detected in significant quantities in an aqueous solution made by cutting open fully discharged cells and immersing them in distilled water. Significant quantities of cyanide were also detected in the sandy loam soil leachate tests using fully discharged cells.

Based upon the results of laboratory data generated in the Phase I study, Versar recommended secured landfills or lined disposal ponds as the only environmentally acceptable disposal alternatives. Disposal recommendations were limited to these methods because of the quantities of cyanide released from discharged cells. However, when these recommendations were made, it was realized that additional laboratory work should be performed.

To assess the environmental consequences of disposal of lithium batteries accurately, it was important to evaluate the effects of discharged lithium cells as they would actually exist under in-use disposal conditions. Data collected during Phase I testing could serve only as an indication of what might exist in actual usage. No information was available to determine how variable the concentrations of these chemical constituents were from cell to cell, or how discharging these cells to different final voltage levels could affect the amount of toxic or hazardous materials potentially available for discharge into the environment.

ECOM officials decided that this information was necessary for their evaluation of lithium cell disposal alternatives. As a result, Phase II testing was initiated to characterize the chemical components potentially released from a lithium cell under various stages of discharge, and to further determine the mobility and adsorption of cell constituents in two soil types of lower permeability. Since no drinking water quality standards exist for either lithium or sulfite, additional work regarding further cell characterization and soil sorption data emphasized the detection of cyanide. The EPA cyanide drinking water standard for water supplies is 0.2 mg/l. The possibility also existed that the chemical composition of the lithium-organic electrolyte/SO₂ cell could be modified to eliminate or greatly reduce the formation of cyanide. This modified cell has an increased SO₂ to lithium ratio than the standard lithium cell.

To evaluate these alternatives, Phase II laboratory testing examined the cyanide concentrations produced by both standard and modified lithium cells at various discharge levels. Soil column leachate tests using fully discharged cells were continued from Phase I using soils of lower permeability and higher sorptive capacity.

To characterize the concentration of cyanide produced in lithium cells under discharge conditions similar to those anticipated during actual usage, cells were discharged to various voltage levels in groups of ten cells per level. This provided data on variations in discharge characteristics and cyanide formation which could be used to evaluate the significance of these variations statistically.

The actual discharge levels chosen for testing were made in conjunction with ECOM personnel after examination of the electrical discharge characteristics of the cells. Sets of ten cells were discharged to various voltage end points using a constant current discharge circuit designed by ECOM.

The results of laboratory analysis with standard cells show that as the discharge state of the cell is increased, the formation of cyanide increases. Cells discharged to a negative voltage condition contained an average of 97.8 mg of cyanide per cell (19.6 mg/l when solubilized in five liters of water), while cells discharged to 1.7 volts contained 22 mg per cell (4.4 mg/l) and at the 2.4 volts level, there was an average of 4.6 mg of cyanide per cell (0.92 mg/l). Live cells which were not discharged contained 1.6 mg per cell (0.32 mg/l).

A comparison of results between discharged standard cells placed in water versus those placed in a high pH buffered solution revealed no statistically different results. The high pH buffer solution was used to minimize possible loss of cyanide to the atmosphere.

Analysis of the modified lithium cells discharged at the 1.7 volt and negative voltage levels, showed that the cyanide production during discharge is minimal. Cyanide analyses revealed no significant difference between the cyanide concentrations at the two levels. The 1.7 volt level cells contained an average of 0.16 mg of cyanide (0.032 mg/l) and negative voltage cells contained only 0.13 mg (0.026 mg/l) of cyanide. The obvious conclusion from these results is that the modified cell apparently eliminates the environmental hazard of cyanide being introduced into the environment during disposal.

The data on the mobility of cell constituents through the soil leachate columns show that the soluble constituents including cyanide leached through the three different soil types at different migration rates, which were primarily dependent upon the porosity of the soil type. The migration rate was fastest through the sandy loam soil (Lakeland) where the maximum lithium, sulfite and cyanide concentrations were detected in a sample after 2,540 ml (40 percent) of the total leachate were collected. This sample contained approximately 13 percent of the total cyanide recovered in the leachate through the sandy loam soil. The migration rate of constituents through silty loam soil (Mattapeake) was slower as evidenced by the detection of a maximum concentration of cyanide after 3,175 ml (66 percent) of the total leachate were collected. This sample represented somewhat of a slug of migrating constituents with almost 17 percent of the total cyanide recovered in this sample. The leachate from the silty clay soil column was even more concentrated. Maximum cyanide levels were observed after 3,300 ml (88 percent) of the total leachate were collected. This sample contained 28 percent of the total cyanide that leached through the silty clay column.

The leachate column test results indicate that no significant adsorption of the soluble cell constituents took place in the soils tested and that although the migration rates through the different soil types varied

considerably, the leachate from all three soil columns contained maximum concentrations of cyanide, lithium and sulfite, which were considerably greater than those considered to be environmentally safe.

Even though the leachate test results showed that environmentally unsafe levels of cyanide will leach through different types of soil, ECOM personnel felt that some type of disposal density model should be developed, which would indicate or predict the number of cells which could be disposed per volume of landfill. Specifically, ECOM was interested in estimating the number of discharged lithium cells which could be disposed of with a volume of solid waste during various scenarios of Army operations without adversely impacting the local environment.

Versar has developed a general model which evaluates the disposal density of lithium cells when incorporated into a sanitary landfill. The model is based upon the volume of precipitation necessary to produce water saturation (field capacity) of the solid waste containing the lithium cell. The model assumes complete dispersion of the lithium cell constituents within the saturated portion of the solid waste. The concentration of constituents in the leachate from the landfill is assumed to be monitored at the bottom of the landfill before it flows into an aquifer. The model cases have been calculated based upon the concentration of cyanide in the leachate at the point of monitoring. The concentration of cyanide has been assumed to be equal to or below 0.2 mg/l which is the EPA designated drinking water standard.

Using the model to predict the worst case situation with a fully discharged standard cell, the volume of solid waste necessary to contain one cell would be 11.9 cubic meters or equivalent to the solid waste produced by 238 Army personnel. Using the model to predict an intermediate case of normally discharged standard cells, the volume of solid waste necessary to contain one cell would be 2.6 cubic meters or equivalent to the solid waste produced by 52 Army personnel.

The development of the simple landfill disposal density model was accomplished to provide ECOM with some rough guidelines of how many cells can be disposed when mixed with solid waste. However, it has been Versar's

experience in dealing with federal and state regulatory agencies that consideration of disposal density factors or dilution factors for contaminants will not stand alone as a rationale for disposal considerations. Additional data must be collected at the actual disposal sites. This requires monitoring of groundwater quality in the immediate vicinity, preferably from monitoring wells located within or adjacent to the landfills.

Versar's recommendations for the disposal of live and discharged standard lithium-organic electrolyte/SO₂ cells are the following:

- The most environmentally safe disposal alternative for the cells is to place them in secured landfills or lined, monitored disposal ponds.
- Sanitary landfills or special landfills can be used where the cells are dispersed in large quantities of solid waste in a carefully controlled manner to produce a leachate containing environmentally safe concentrations of cyanide. However, this disposal practice should be used only with landfills where leachate monitoring is practiced on a routine basis.

Versar's recommendation for the disposal of the modified lithium-organic electrolyte/SO₂ cell is that the cell can be disposed of with the normally collected solid waste in a sanitary landfill. The potential environmental effects posed by disposal of the modified cell are considered to be minimal.

II. TECHNICAL RESULTS AND DISCUSSION

A. Description of the Components of the Lithium Organic-Electrolyte/ SO₂ Cells and Environmental Considerations of Disposal.

Inasmuch as some of the constituents of the lithium organic-electrolyte/ SO₂ cells present a toxic or hazard potential, it was necessary to assess the environmental consequences of disposal. The composition of the cell and the toxicological and hazardous properties of its constituents as they relate to disposal options are presented in the following sections.

1. Description of the Cell

The lithium organic-electrolyte/SO₂ cell is a new primary cell having several advantages over existing cells. These advantages include higher voltage, longer shelf life, better low temperature performance, higher capacity, greater power densities, and lighter weight.

Chemically the lithium organic-electrolyte/SO₂ contains lithium metal as the basis for the anodic half reaction ($2\text{Li} \rightarrow 2\text{Li}^+ + 2\text{e}^-$) with sulfur dioxide as the cathode (half reaction, $2\text{SO}_2 + 2\text{e}^- \rightarrow \text{S}_2\text{O}_4^{=}$). Thus, the overall electrochemical reaction is $2\text{Li} + 2\text{SO}_2 \rightarrow \text{Li}_2\text{S}_2\text{O}_4$. The electrolyte matrix is non-aqueous since lithium reacts vigorously with water to generate hydrogen gas and heat. The electrolyte is an organic liquid containing an anhydrous soluble salt. The electrolytes which have been used include acetonitrile and propylene carbonate. The salt used in the electrolyte is lithium bromide.

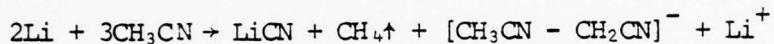
Under discharge conditions, the dissolved SO₂ is reduced to sulfite at the cathode as the metallic lithium anode is converted to lithium ions. As a result, discharged cells contain organic electrolyte with dissolved lithium salts and sulfites.

In the laboratory investigations conducted under this project, two chemically different sets of cells were examined. Basically these cells differed from one another in SO₂ to lithium ratios only. The composition of a standard lithium organic-electrolyte/SO₂ D-cell is as follows:

1. Lithium anode - 4.2 grams
2. Carbon cathode consisting of an aluminum support screen, and 80% acetylene black/20% teflon mixture - 13 grams.
3. Polypropylene separator - 1.0 gram,
4. Electrolyte consisting of 24.5 grams of sulfur dioxide, 2 grams of lithium bromide, and 8.5 grams of acetonitrile.

The second set of cells, classified as LO 26 SX (Modified) contains a higher SO₂ to lithium ratio than the standard cells.

In addition to the electrochemical reaction and the resultant formation of Li₂S₂O₄ some breakdown of acetonitrile to cyanide occurs. This reaction apparently becomes important as the SO₂ is depleted. The reaction postulated as the source of cyanide is:



The detectable species is probably lithium cyanide (LiCN) due to its relatively high solubility.

2. Cell Component Toxicity Description

Several constituents and products of the electrochemical reaction of the cell are known to have toxic or hazardous properties, thus affecting the selection of acceptable disposal methods. A thorough literature review of the toxicity and hazardousness of these constituents was conducted in Phase I and the results are summarized below. Complete toxicity profiles were presented in the Phase I Report.² On the bases of this toxicity review, carbon, teflon and polypropylene were found to be insignificant in their environmental effect and therefore, do not affect disposal considerations.

Lithium and its Compounds

Metallic lithium (Li) and lithium bromide (LiBr) are components of the battery. Two other lithium compounds were also studied: lithium hydroxide (LiOH), which is formed by the reaction between lithium and water; and lithium dithionite (Li₂S₂O₄), which occurs as a result of the chemical oxidation of lithium and reduction of sulfur dioxide during battery discharge.

The toxicity of metallic lithium was not considered germane to this study because it reacts immediately on contact with water or water vapor to form LiOH and hydrogen gas. Lithium hydroxide is a strong base

and quite toxic due to its corrosive action on skin and internal tissues. An increase in pH will occur when it is dissolved in water. This increase could prove to be harmful to aquatic and soil biota. Lithium dithionite ($\text{Li}_2\text{S}_2\text{O}_4$) forms a slightly alkaline solution in water which is corrosive to skin. No toxicity data are available for $\text{Li}_2\text{S}_2\text{O}_4$, but data on $\text{Na}_2\text{S}_2\text{O}_4$ (sodium dithionite) indicate that the $\text{S}_2\text{O}_4^{=}$ group is practically non-toxic to mammals. Lithium bromide (LiBr) is also practically non-toxic to mammals. The major groups of organisms threatened by the lithium compounds are plants and freshwater invertebrates. Very small amounts (1-30 mg/l) of lithium compounds when added to soil have caused toxic effects to a variety of plants, especially citrus. Concentrations of lithium salts as low as 7.2 mg/l have immobilized freshwater invertebrates. Lithium metal can also cause an airborne hazard when it reacts with water, releasing explosive hydrogen gas.

Sulfur Dioxide and Sulfurous Acid

Sulfur dioxide (SO_2), a gas, is toxic to plants, mammals, fish and insects. Concentrations in air of less than 1 ppm have caused toxic effects in plants.

In mammals, the harmful effects of SO_2 are due to physical damage to the lungs and other mucoseroous membranes. In contact with water (or mucous), SO_2 forms sulfurous acid (H_2SO_3) which corrodes the tissue.

The formation of H_2SO_3 is also the mechanism by which SO_2 exerts toxic effects on fish and other aquatic life. During laboratory investigations sulfite analysis was used as an indication of sulfurous acid and its salts which potentially could be released from a lithium cell into the environment.

Acetonitrile

Acetonitrile is another potentially hazardous cell component, since, it also is flammable. The exothermic reaction between metallic lithium and water could theoretically supply the heat required to ignite acetonitrile, resulting in the possibility of fire or explosion. Inhalation of acetonitrile vapors in some reported cases has resulted in death. However, it does not represent a serious airborne problem since extremely high concentrations

are required to cause toxic effects. Acetonitrile has been found to be essentially non-toxic to mammals, fish, birds and amphibians. The major toxicological consideration associated with this compound is its potential decomposition to an inorganic cyanide radical.

Cyanide

Although cyanide is not a component of the cell, it was found in significant concentrations in discharged standard cells due to disassociation of acetonitrile upon SO_2 depletion. Cyanide is acutely toxic to mammals, fish, invertebrates, protozoa, plants and bacteria. The cyanide ion is less acutely lethal than hydrogen cyanide. It interferes with enzymes associated with the cellular oxidation process, and in effect asphyxiates the cells. Cyanide is not biologically accumulated and at sub-toxic dosages it is rapidly catabolized to relatively non-toxic substances (e.g., thiocyanate). Hydrogen cyanide (HCN) and most cyanide salts are extremely soluble in water. In addition, HCN is both volatile and flammable, presenting problems in handling.

Propylene Carbonate

Propylene carbonate ($\text{C}_3\text{H}_4\text{CO}$) may represent a handling problem since it is flammable. However, it is practically non-toxic to mammals and is only slightly soluble in water.

The toxicological evaluation presented above indicates that the standard lithium organic-electrolyte/ SO_2 cell contains several substances which can cause serious environmental problems. Specifically, these problems are: (1) release of toxic or hazardous compounds to sources of drinking water; (2) release of toxic gases; and (3) fire or explosion hazard. In assessing the consequences of disposal of cells the following points must be considered:

- When discharged, standard cells contain appreciable amounts of cyanide which are extremely toxic to all life forms;
- Plants or livestock may be harmed by sulfur dioxide or lithium ions; and
- Acetonitrile or propylene carbonate could be ignited by the heat of reaction between metallic lithium and water, or other heat sources in the presence of oxygen, which could result in a fire or explosion.

Table 1 gives a qualitative rating of the toxicity and hazard of each of the compounds found in lithium organic-electrolyte/SO₂ cell. The rating is based on a qualitative assessment of the toxicity of the components with respect to the concentrations likely to result from cell disposal.

3. Environmental Considerations of Disposal

Results of the toxicity review performed during Phase I of this investigation indicated that certain cell components have potentially toxic effects. The disposal of standard cells could impact the environment via one or more of the following vectors:

- (a) Contamination of surface/or groundwaters;
- (b) Contamination of soil and vegetation; and
- (c) Release of amounts of HCN and SO₂ to the atmosphere.

The degree to which one or all of these consequences could occur depends upon the disposal method and the potential toxic load introduced into the environment. The following section is a review of the environmental considerations to be addressed in assessing specific disposal options.

Inherent to several disposal methods are certain technical difficulties that would need to be overcome. For example, implementation of certain methods would necessitate segregation of cell constituents into soluble and insoluble phases. This pre-condition for disposal would require the development of a safe method for opening cells, in addition to assessment of environment effects.

Land disposal is the most frequently used and the least costly method of disposing of solid wastes in the United States. Actual methods range from open dumping to a sophisticated waste-specific

TABLE 1. QUALITATIVE TOXICITY AND HAZARD POTENTIAL FOR LITHIUM BATTERY COMPOUNDS

<u>Compound</u>	<u>Toxic to Plants</u>	<u>Toxic to Aquatic Animals</u>	<u>Toxic to Mammals (incl. humans)</u>	<u>Airborne Toxin or Hazard</u>	<u>Handling Hazard</u>
Acetonitrile	u.k. ¹	No	No	No	Yes
CN ⁻	Yes	Yes	Yes	No	Yes
HCN	Yes	Yes	Yes	Yes	Yes
Li metal	Yes	Yes	Yes	Yes	Yes
Li ⁺	Yes	Yes	No	No	No
Br ⁻	u.k. ¹	No	No	No	No
S ₂ O ₄ ⁼	u.k. ¹	No	No	No	No
OH ⁻	Yes	Yes	Yes	No	Yes
Propylene Carbonate	u.k. ¹	u.k. ¹	No	No	Yes
SO ₂	Yes	Yes	Yes	Yes	Yes
H ₂ SO ₃	Yes	Yes	Yes	No	Yes

¹Unknown - Information on toxicity for this group is not in published literature.

chemical fixation process. The practice of indiscriminate land disposal fails to control potentially toxic emissions, runoff and leachate, and has possible detrimental effects resulting from waste interactions. This is especially true of the practice of open dumping. Currently, controlled landfilling of waste materials is a much more effective means of minimizing these problems. Despite this fact, landfilling per se does not assure protection from all the hazards associated with standard lithium cell disposal.

Landfill methods, however, are amenable to standard lithium cell disposal provided specific conditions are met. Monitoring wells and leachate treatment provisions may be required to protect groundwater from contamination. In addition to these controls, segregation of wastes and the recording of burial coordinates may also be necessary to limit any chemical interactions within the landfill or resultant leachate.

Basically, there are two methods of landfilling which could be considered when disposing of standard lithium cells. The first is a secured landfill which retards the percolation of hazardous materials through the landfill to insure that the groundwater integrity in the area is maintained. This can be accomplished by locating secured landfills in areas with impervious soil substrates. (A criterion for secured landfills is permeability of soil of less than 10^{-7} cm per second).³ If impermeable soils are not available, then plastic or other materials would be needed as liners to trap potentially hazardous leachate. There are also certain modifications available to this type of secured landfill which would retard leaching by isolating the wastes. These modifications would include:

- Capping the waste with an impervious material such as asphalt or concrete;
- Total encapsulation of the lithium cells in an impervious material; and
- Placing cells in steel drums followed by burial of the drums.

At best, these modifications offer only short term containment since degradation is always possible.

A second landfill method applicable to lithium cell disposal would be to control the number of disposed cells in a given area of a landfill. A carefully controlled disposal density might be used to insure that any leachate from the landfill contained only insignificant concentrations of hazardous cell components. Establishing this disposal density guideline would require complete understanding of soil/cell component interactions, constituent diffusion through different waste or soil types, as well as the levels of materials potentially released from each cell into the environment.

Several disposal alternatives to landfills are based upon dissolution of cell components into an aqueous medium and the containment or treatment of the resultant liquor. These alternatives include use of disposal ponds or lagoons, deep well injection and disposal via municipal sewers.

Disposal ponds or lagoons are frequently used to dispose of some types of hazardous waste. However, there are some critical factors to be considered to insure protection of surface and groundwater against contamination. Surface waters play an important role in recreational activity and as sources of drinking water in addition to supporting a delicately balanced ecosystem. Thus, it is essential that they be protected from accidental contamination due to disposal pond overflow or direct discharge. Concentrations of 0.21 mg/l HCN and 0.5 mg/l H₂SO₃, for example, have been reported to be fatal to fish.^{4,5} Adverse effects such as heavy rainfall events must be anticipated and appropriate flood and runoff controls must be provided.

To prevent infiltration and contamination of groundwater, impervious materials such as clay, plastic, concrete or epoxy must be used to line the pond. Even with the most careful construction, however, cracks and leaks do occur and therefore, a monitoring or detection system must be incorporated into this type of disposal regime.

Even with these safeguards, volatile substances may escape to the atmosphere representing a serious airborne danger. Air quality standards

for both HCN (10 ppm) and SO₂ (0.03 ppm) might be exceeded unless the total number and rate at which cells are placed in the pond are controlled.⁶ An additional threat to the environment may be the actual physical presence of the pond or lagoon. Unless enclosed or covered, the pond may adversely effect wildlife (e.g. migratory waterfowl) attempting to use these waters.

Deep well injection is a specialized form of land disposal of hazardous wastes. It is normally restricted to liquids only, since suspended solids or sludges tend to clog the porous rock or sand into which they are being injected. To utilize this method, a suitable containment well must be found in which hazardous wastes can be permanently stored and contamination of groundwater supplies will not occur. Deep well injection will require opening the cell, dissolving the soluble components, and disposal of the remaining solid fraction. This would be a technically difficult method for disposal of standard lithium cells.

Disposal of industrially generated soluble substances is commonly accomplished by discharging them into municipal sewers for treatment at sewage treatment plants. Several considerations are necessary when evaluating the application of this method to lithium cell disposal. The first is the problems associated with opening the cells. The second consideration would be the possible effects this waste could have on the microbes within the municipal treatment plant essential to the organic digestion process. Inhibition of these organisms has been reported to occur at cyanide concentrations of less than 4 mg/l, and would result in rendering the plant ineffective in sewage treatment.⁷

Incineration is a method commonly used to dispose of combustible solid wastes. Specific considerations to be addressed in assessing the applicability of incineration to the lithium cell would be:

- Release of HCN, SO₂ and volatile lithium to the atmosphere.
- Since incineration must be preceded by cell opening, escaping gases (SO₂) must be contained to avoid injurious effects.

- Nickel-plated steel casings are not acceptable for incineration and must be disposed of separately, thus compounding disposal procedures.

To comply with air quality standards, combustion products, HCN, SO₂ and volatilized lithium would have to be eliminated or greatly reduced by scrubbing of stack emissions. A second approach to maintaining safe levels of these cell constituents would be to control the ratio of cell related waste to non-cell waste entering the incinerator (and thus limit gas emission concentrations of these components). The practical problems inherent in opening lithium cells previous to incineration make this disposal method difficult to achieve.

Recovery and reuse is considered to be the most environmentally desirable method of 'disposing' of wastes. Not only does it reduce the pollution problem associated with conventional disposal methods, but it also diminishes the need for extraction of the resource from the natural source. It has been demonstrated that lead, silver, mercury, cadmium and other heavy metals can be recovered from various battery types. However, many components of the lithium cell are not amenable to recovery and must be disposed of. Technical problems associated with lithium cell opening also would be maximized in a recovery and reuse program.

Although the major environmental considerations of various disposal regimes have been addressed, additional economic and logistical constraints may exist. These factors must also be examined before any disposal procedures are adopted.

To quantify these environmental considerations and assess the environmental consequences of disposal of lithium batteries, laboratory tests characterizing the chemical constituents of lithium batteries was necessary. Specific information regarding the solubility of these constituents and amounts of lithium, sulfite, and cyanide contained in the cell or produced during its discharge had to be obtained. In addition, data was needed on the mobility and adsorption of cell constituents in various soil and sediment types. To obtain this information extensive laboratory investigations were performed. The results of these investigations and how they related to the assessment of disposal alternatives

are presented in the following section.

B. Discharge of Lithium Cells and Analysis of Cell Constituents in Aqueous Media.

Introduction

To evaluate the environmental impact of the disposal of lithium batteries, it was important to characterize the chemical components or by-products potentially released from a lithium cell. Laboratory investigations were conducted to determine:

- the identification of those cell constituents which are present in water;
- the level of dissolution of cell constituents in water;
- the extent to which known quantities of these constituents or by-products would be adsorbed by three soil types; and
- the mobility and adsorption of these cell components in leachate columns containing three types of soil.

An estimate of the types and quantities of compounds released into an aqueous media through dissolution of lithium cell constituents was made by submerging cross-sectioned discharged cells in distilled water. A stainless steel vessel containing five liters of water was used for each cell. This volume of water guaranteed that dissolution of all soluble components occurred, and that no precipitation of the chemical compounds was possible as a result of saturation of the solution.

Known quantities of solutions containing opened cells were added to three different soil types. Samples of these solutions were analyzed for various chemical constituents to determine the adsorption of cell constituents or by-products in soils. These soil-water samples were then shaken and allowed to stand prior to filtering. Analysis of the filtrate samples was then performed and the differences between the concentration of original solution and filtered solution was estimated to be the adsorption capacity of those soils.

It was also important to determine the effect different soil types would have on the concentrations of standard cell constituents in water percolating through the soil, to evaluate the environmental impact of the land disposal of lithium batteries. Leachate tests were performed to assess the mobility and transport of toxic or hazardous materials, and the degree to which they were absorbed by soils. These tests consisted of comparisons between concentrations of cell constituents in leachate and the levels solubilized in distilled water testing. Three different soil types were selected for this evaluation. These laboratory procedures and results were detailed in the Phase I Report.

Standard lithium cells were evaluated in Phase I of this program under live (no discharge) and discharged conditions. Discharge of these cells was accomplished with a resistance circuit for 72 hours. The discharge circuit included a 5 ohm resistance between a "D" cell holder containing one standard lithium cell. During discharge the cell's voltage was periodically monitored and the circuit resistance checked.

Following discharge these cells were placed in liquid nitrogen for 30 minutes to reduce the internal pressure within the cell from about three atmospheres to one atmosphere. This was done principally to reduce the amount of SO_2 vaporization during opening. Cells were then cut in half longitudinally using a mechanical saw in a closed fume hood. Upon opening, the cells were either dropped into separate vessels of water (for the solubility and adsorption test) or embedded in the soil columns. Chemical analysis of the solutions was limited to those components which were rated as toxic or potentially hazardous when present in the environment.

1. Phase I Results

Phase I laboratory testing was performed to determine the concentration (solubility) of acetonitrile, lithium and sulfite in solutions prepared from cross-sectional live and discharged standard lithium cells, and to evaluate how the level of these components might change with increased exposure time to an aqueous media.

Cyanide analysis was also performed at that time. In spite of the fact that free cyanide was not a component of lithium cell, it might be present in water or leachate samples as the result of acetonitrile CH_3CN breakdown to cyanide ions (CN^-). Analysis for acetonitrile was discontinued when the presence of large concentrations of cyanide from a discharged cell was discovered, since cyanide became the predominant environmental consideration.

Cyanide was found in solutions containing discharged standard lithium cells, with an average of 160 mg per cell introduced into solution. Some variation in the cyanide concentration of these water solutions was observed. The concentrations generally increased to their maximum level in samples collected 24 hours after the discharged cells were opened. Live cells contained less than 0.5 mg per cell of soluble cyanide, with all samples extracted from the five liter solution containing less than 0.1 mg/l cyanide.

Discharged cells when submerged in distilled water for 144 hours emitted 2,590 mg per cell of soluble lithium. Increasing amounts of lithium were dispersed into the aqueous media throughout the test period with concentrations reaching 1,076 mg/l in samples collected 144 hours after the discharged cells were opened. Live cells emitted 3,365 mg per cell of soluble lithium. A similar pattern of increased dissolution of lithium with longer aqueous media exposure was also observed for live cells.

Discharged standard cells contributed an average of 5,360 mg per cell of sulfite to the water solution. Samples collected from vessels containing standard live cells indicated that 14,150 mg per cell of sulfite were solubilized from these cells.

Results of soil-sediment adsorption testing revealed that an insignificant quantity of lithium cell components were absorbed by the three soil types. Concentrations generally were reduced by less than two percent.

Data collected from leachate testing of discharged standard cells placed in a sandy loam soil column indicated that lithium concentrations

reached a maximum level of 1,999 mg/l, sulfite 11,100 mg/l, and cyanide 39.0 mg/l in leachate collected during Phase I testing. Breakthrough of lithium cell components was not observed during this period in either silty loam or silty clay columns.

Phase I laboratory testing showed:

- that many of the lithium battery constituents are quite soluble in water;
- that cyanide was detected in significant concentrations in a solution in which an opened discharge cell was placed;
- that significant quantities of lithium cell constituents can be transported through sandy loam soil; and
- that the concentration of cyanide in the leachate from the sandy loam soil column represented an environmental and health hazard.

Based upon the data available at that time for the toxic and hazardous properties of the cell, it appeared that the best options suitable for disposal of lithium cells were secured landfills or controlled disposal ponds. Federal water quality criteria have established standards for cyanide in freshwater (drinking supply) of 0.2 mg/l.⁸

However, to assess the environmental consequences of disposal of lithium batteries accurately, it was important to evaluate the effects of discharged lithium cells as they would actually exist under natural disposal conditions. Data collected during Phase I testing could serve only as an indication of what might exist in actual usage. No information was available to determine how variable the concentrations of these chemical constituents were from cell to cell, or how discharging these cells to different final voltage levels could affect the amount of materials available for discharge into the environment.

ECOM officials decided that this information was pertinent to their evaluation of lithium cell disposal alternatives. As a result, Phase II testing was initiated to fully characterize the chemical constituents potentially released from a lithium cell and to determine the mobility

and adsorption of cell constituents in the remaining two soil types. Since no drinking water quality standards exist for either lithium or sulfite, additional work regarding further cell characterization and soil sorption data emphasized the detection of cyanide. Lithium battery developmental research indicated that the production of cyanide within the cell was a function of chemical reactions which occurred during its discharge (See Section IIA). As cells were further discharged (increased amp-hours of use), formation of cyanide was increased. The possibility also existed that the chemical composition of the lithium organic-electrolyte/SO₂ cell could be modified to eliminate or greatly reduce the formation of cyanide. To evaluate the alternatives available, Phase II laboratory testing examined, at various discharge levels, both standard and modified lithium cells.

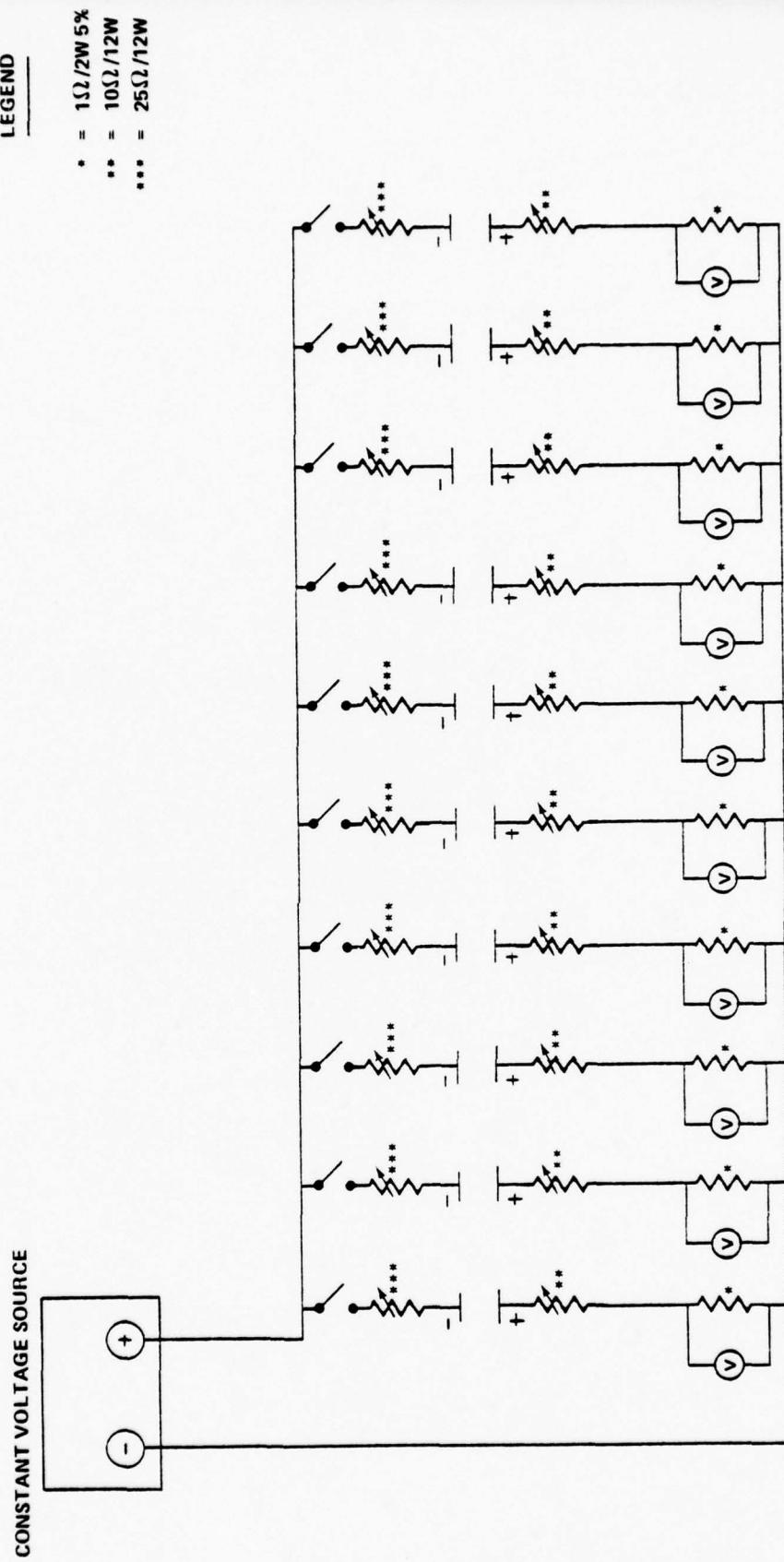
2. Testing of Cells Discharged to Various Levels

Additional standard cells and modified cells were tested in Phase II of the program, to characterize the concentration of cyanide produced in lithium cells under discharge conditions similar to those anticipated during actual usage. Cells were discharged to various voltage levels in groups of ten cells per level. This provided the necessary data on variations in discharge characteristics and cyanide formation among similarly treated cells. It also permitted a statistical evaluation of the significance of these variations.

Description of Discharge Test Circuit and Procedure

The simultaneous discharge of ten lithium cells was conducted using a test circuit specifically designed and recommended by ECOM for this program. Cells needed to be discharged under controlled laboratory conditions and in a manner that most closely represented actual application and usage of the cell to assess environmental impacts properly. The test apparatus consisted of ten discharge circuits connected in parallel. Each circuit included a cell holder, two variable resistors (one on each side of the cell) and a 1 ohm resistor across which the current discharge of the cell was monitored (See Figure 1). As each lithium cell was

FIGURE 1 DISCHARGE TEST CIRCUIT APPARATUS



discharged, the resistance in the circuit changed. Constant current discharge of the cell was maintained by adjusting the variable resistors in the circuit to a different resistance level. A reference voltage circuit, which was monitored continuously along with the ten discharge circuits (See Figure 2), was also included in the test circuit. A constant voltage source was applied to the test circuit throughout the discharge period.

Actual discharge procedures utilized during Phase II are described in the following steps:

- Lithium cells were placed in cell holders and soldered into place in the test circuit;
- The discharge rate was set at 0.5 amp for each cell by adjusting a power supply and the discharge circuit variable resistors;
- Voltage across the 1-ohm resistors was recorded on a multi-point recorder to indicate the current flow through each circuit;
- The reference circuit was set at 0.4 volts and was monitored on a continuous basis to insure the accuracy of the discharge readings;
- Voltage from a power supply source was applied to the test apparatus and one-by-one each circuit was opened. Generally this voltage was between 13 and 15 volts depending on the actual number of lithium cells being discharged;
- Final adjustments were made to the variable resistors to obtain a 0.5 amp discharge on each cell;
- Voltage across one of the discharging cells was monitored on a continuous basis with an additional D.C. recorder;
- Voltage across the remaining cells was monitored every 15-20 minutes once the voltage dropped below 2.7 volts;
- As cells continued to discharge, the frequency of cell voltage monitoring was increased to guarantee that discharge of the cells was terminated at the prescribed end point;

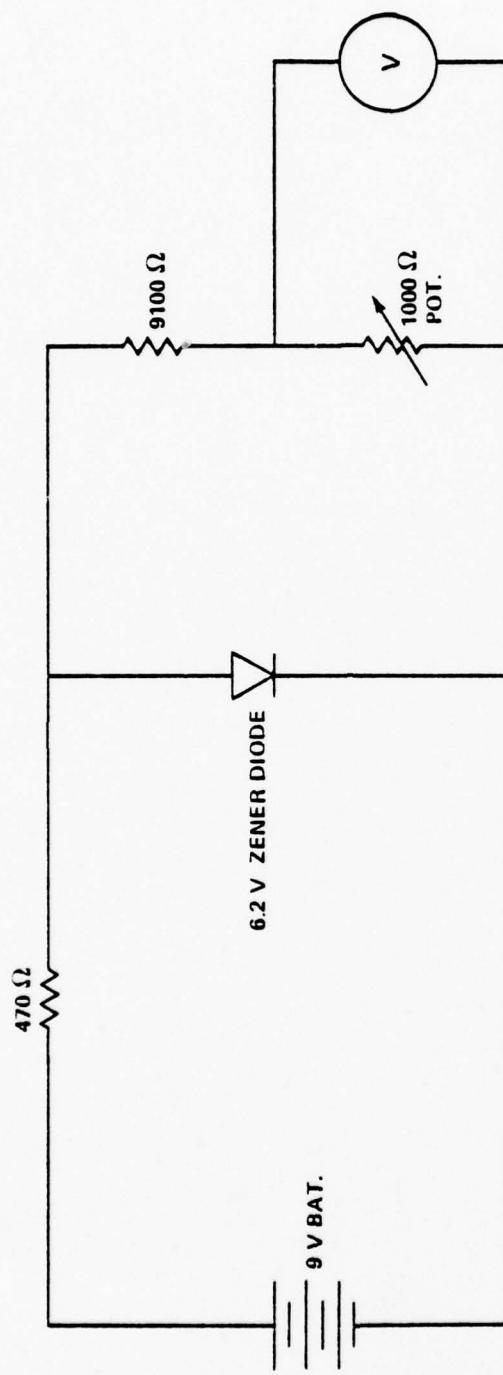


FIGURE 2 REFERENCE VOLTAGE CIRCUIT

- At the end point the circuit was closed and the cell removed from the cell holder and placed in liquid nitrogen;
- Voltages across the 1-ohm resistors of the remaining cells were checked and readjusted to 0.5 volts if necessary; and
- Amp-hours of discharge were calculated from recorder print-out and data book recordings.

Figure 3 illustrates a cell discharge test in progress, including the test circuit apparatus, voltage source and recorders.

Cell opening and sample collection procedures were similar to those used during Phase I of this program and were detailed in that report.⁹ Samples were collected 24 and 48 hours after the cells were opened from the aqueous solution and preserved for cyanide analysis.

Summary of Discharge Levels

Sets of ten standard and modified lithium cells were discharged to various voltage levels. The actual discharge levels chosen for testing were made in conjunction with ECOM officials after examination of the electrical discharge characteristics of the cells. Figures 4 and 5 represent actual discharge curves for standard and modified lithium cells. As depicted in these figures, the 1.7 volt level is a point at which the voltage is dropping rapidly (with almost a vertical slope). ECOM personnel indicated that this was the level, in most applications, where equipment containing lithium cells became marginally operable. To evaluate this further, two discharge levels were selected above, 2.4 and 2.0 volts, and below, 0.1 and negative volts, the 1.7 volt level. Sets of ten standard cells were discharged at these five levels. In addition, sets of ten cells were discharged at both the 1.7 and 0.1 volt levels and placed in vessels containing 5 liters of $\text{Na}_2\text{HPO}_4/\text{NaOH}$ buffer solution. The buffer maintained these solutions at pH 12 throughout the 48 hour period and minimized any volatilization of hydrogen cyanide. Samples were taken from each buffered solution after 24 and 48 hours and analyzed for cyanide to compare with non-buffered solution data.

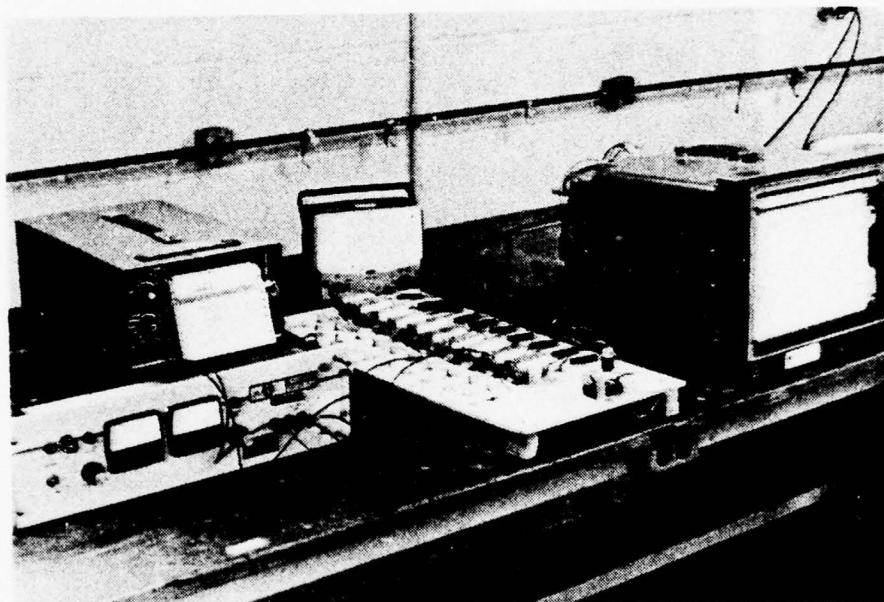


FIGURE 3 DISCHARGE TESTING OF LITHIUM CELLS

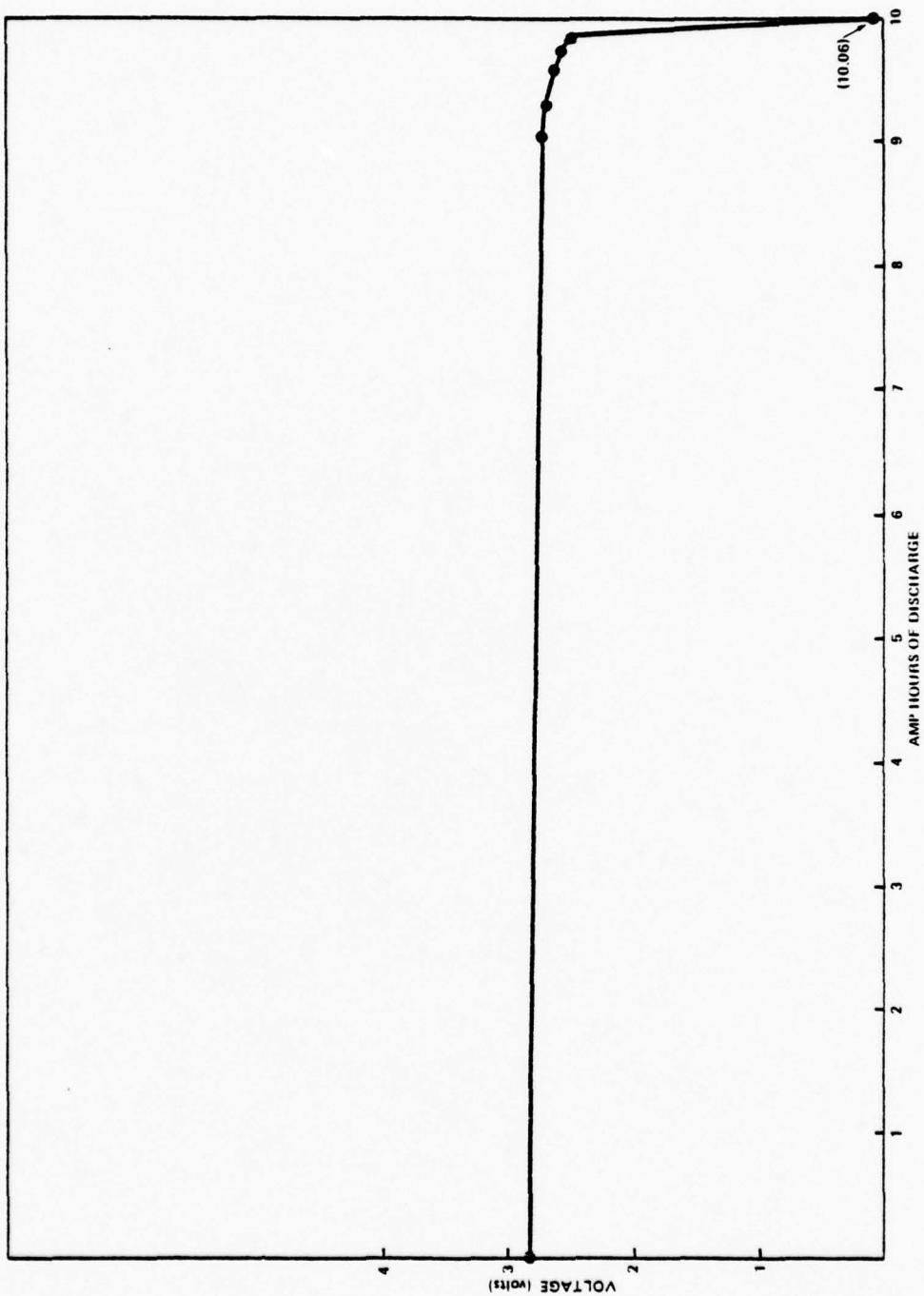


FIGURE 4 STANDARD CELL DISCHARGE CURVE

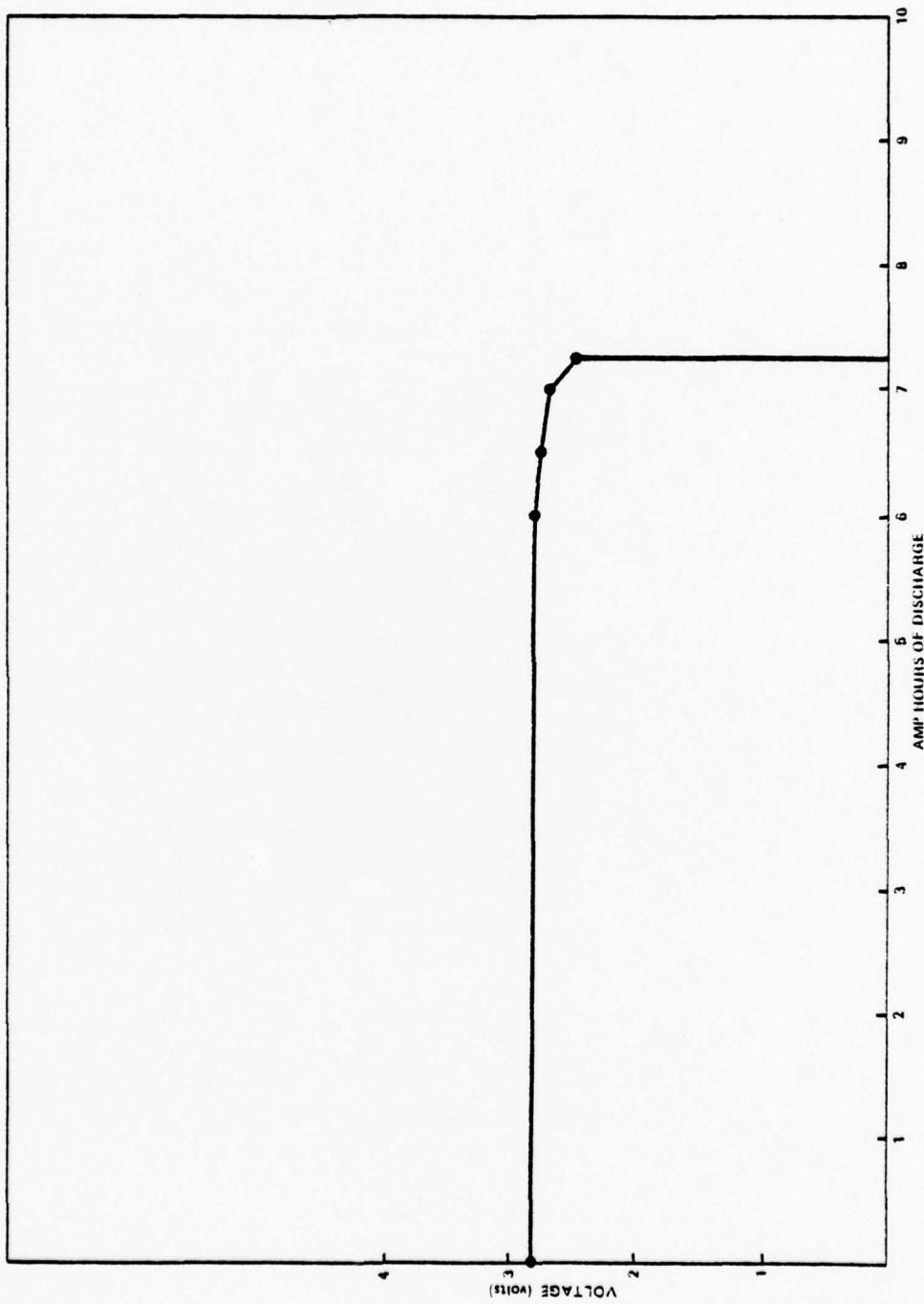


FIGURE 5 MODIFIED CELL DISCHARGE CURVE

To evaluate whether lithium cells which had a modified chemical composition from the standard cells eliminated or greatly reduced the formation of cyanide, ten modified cells were tested at the 1.7 volt and negative voltage levels and compared to standard cells discharged similarly. The following section will detail the results of analytical testing and statistical evaluations of these standard and modified lithium cells at the various discharge levels.

3. Analysis of Cell Components in Aqueous Media

Analytical Procedures

Laboratory analyses of solutions containing standard or modified lithium cells were performed by procedures summarized in Appendix A. All methods utilized during this program are approved by EPA for analysis of water samples.¹⁰ Separate samples were collected and preserved for each chemical constituent held for analysis (more than one hour after sample collection) and incubated at 4°C.¹¹

Summary of Analytical Results

When the period of discharge is increased or the end point voltage level is decreased, an increased production of cyanide occurs within the standard lithium cell. Cells discharged to negative voltage contained an average of 97.8 mg of cyanide (19.56 mg/l in solution) while cells discharged to 1.7 volts contained 22 mg (4.4 mg/l) and at 2.4 volts, 4.6 mg of cyanide (0.92 mg/l). A summary of the mean level of soluble cyanide per cell is presented in Table 2.

Comparison of results between discharged standard cells placed in water versus those placed in buffered solution revealed no consistent pattern of variation. Samples containing cells discharged to 1.7 volts contained an average of 4.4 mg/l cyanide in water and 9.7 mg/l in buffered solution. At the 0.1 volt discharge level, cyanide concentrations were reported at 16.9 mg/l in water and 7.8 mg/l in buffered solution. Results of individual analysis of discharged standard lithium cells are detailed in Appendix Tables B-1 through B-8.

TABLE 2. AVERAGE CYANIDE PER STANDARD LITHIUM CELL SOLUBLE IN AN AQUEOUS MEDIA AFTER 24 HOURS AT DIFFERENT DISCHARGE LEVELS

<u>Discharge Level (Volts)</u>	<u>Average Cyanide per Cell (mg)</u>
2.84 (no discharge)	1.6
2.40	4.6
2.00	28.0
1.70	22.0
0.10	84.5
-3.88 (Mean)	97.8

Cyanide concentrations of standard cells were compared with their discharge level and actual amp-hours of discharge (use). This data is shown in Table 3 and Figures 6 and 7. Based on these results, it appears that the same general relationship exists between increased amp-hours of discharge and the cyanide produced within the standard lithium cell as was found with the discharge voltage.

Modified lithium cells discharged at the 1.7 volt and negative voltage levels and analyzed, indicate that the cyanide production during discharge is minimal. Results of cyanide analysis revealed no significant difference in the cyanide concentrations at the two levels tested. The 1.7 volt cells contained an average of 0.16 mg of cyanide (0.032 mg/l) and negative voltage cells 0.13 mg (0.026 mg/l). Comparisons of standard versus modified cyanide levels are presented in Table 4. Note the reduced amp-hours (use) of the modified cells necessary to achieve similar voltage discharge levels.

The soluble constituents from discharged standard cells had pH values above 11.4. Soluble live cell components had a mean pH value of 6.74.

TABLE 3.

SUMMARY OF RESULTS OF ANALYSES
OF STANDARD AND MODIFIED LITHIUM
CELL SAMPLES

<u>Discharge Level (Volts)</u>	<u>Discharge Level (Average Amp Hrs)</u>	<u>Average pH of Samples</u>	<u>Average Cyanide Concentration (mg/l)</u>
<u>Standard Cells in Water</u>			
2.84 (no discharge)	0.00	6.74	0.32
2.40	8.29	11.73	0.92
2.00	9.50	11.78	5.6
1.70	9.55	11.47	4.4
0.10	10.55	11.83	16.9
-3.88 (Average)	10.27	12.59	19.6
<u>Standard Cells in Buffer</u>			
1.70	9.69	12.00	9.7
0.10	9.50	12.00	7.8
<u>Modified Cells in Water</u>			
1.70	7.25	4.18	0.032
-3.84 (Average)	8.44	4.76	0.026

TABLE 4.

COMPARISON OF SOLUBLE CYANIDE PRODUCED
IN DISCHARGED STANDARD AND MODIFIED
LITHIUM CELLS

<u>Lithium Cell Type</u>	<u>Discharge Level (Volts)</u>	<u>Amp Hours (Use)</u>	<u>Average Cyanide Concentration (mg/l)</u>	<u>Average Cyanide per Cell (mg)</u>
Standard	1.70	9.55	4.40	22.0
Modified	1.70	7.25	0.032	0.16
Standard	-3.88 (Average)	10.27	19.56	97.8
Modified	-3.84 (Average)	8.44	0.026	0.13

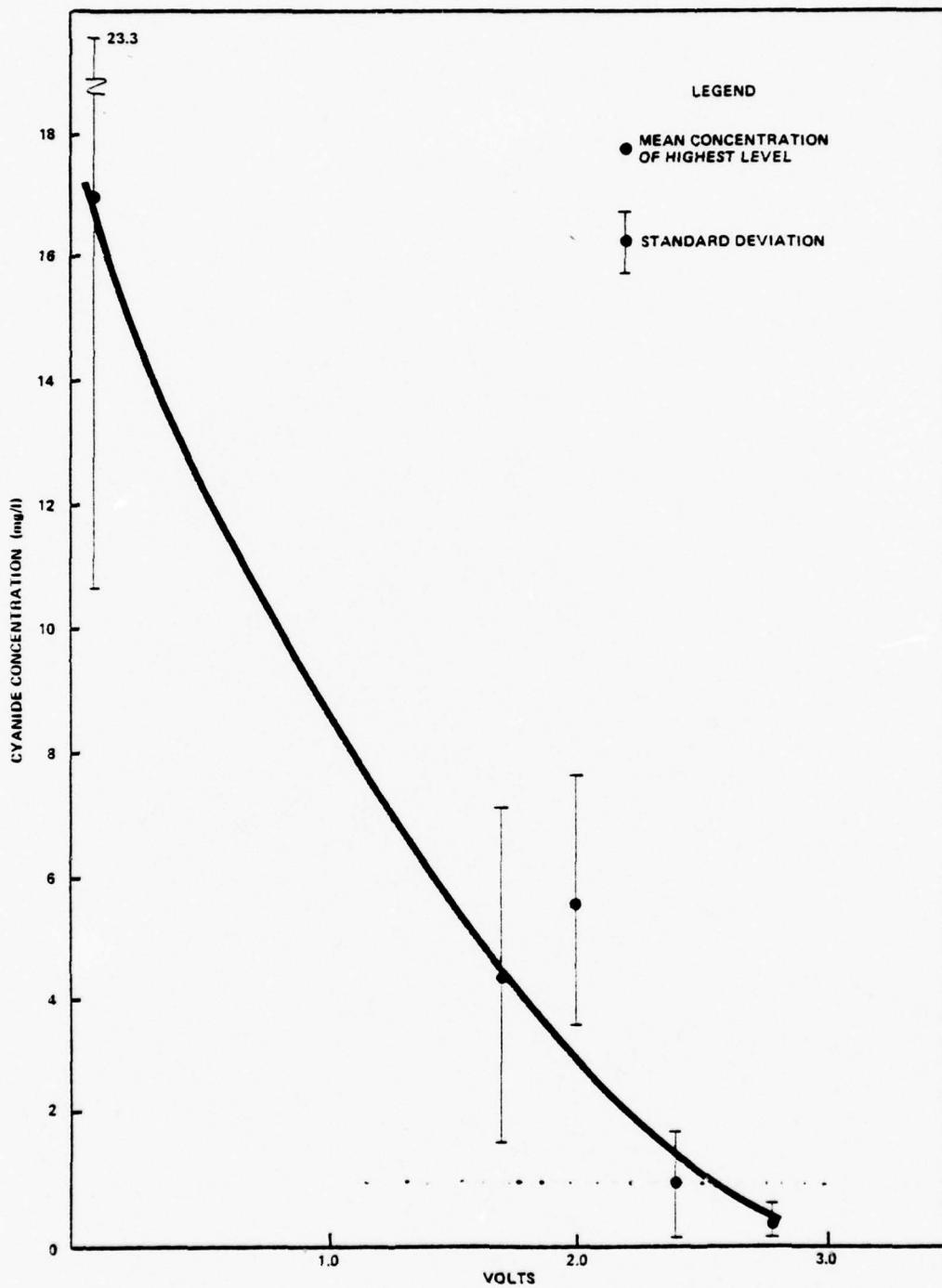


FIGURE 6 CYANIDE CONCENTRATION OF LITHIUM CELLS vs. FINAL VOLTAGE

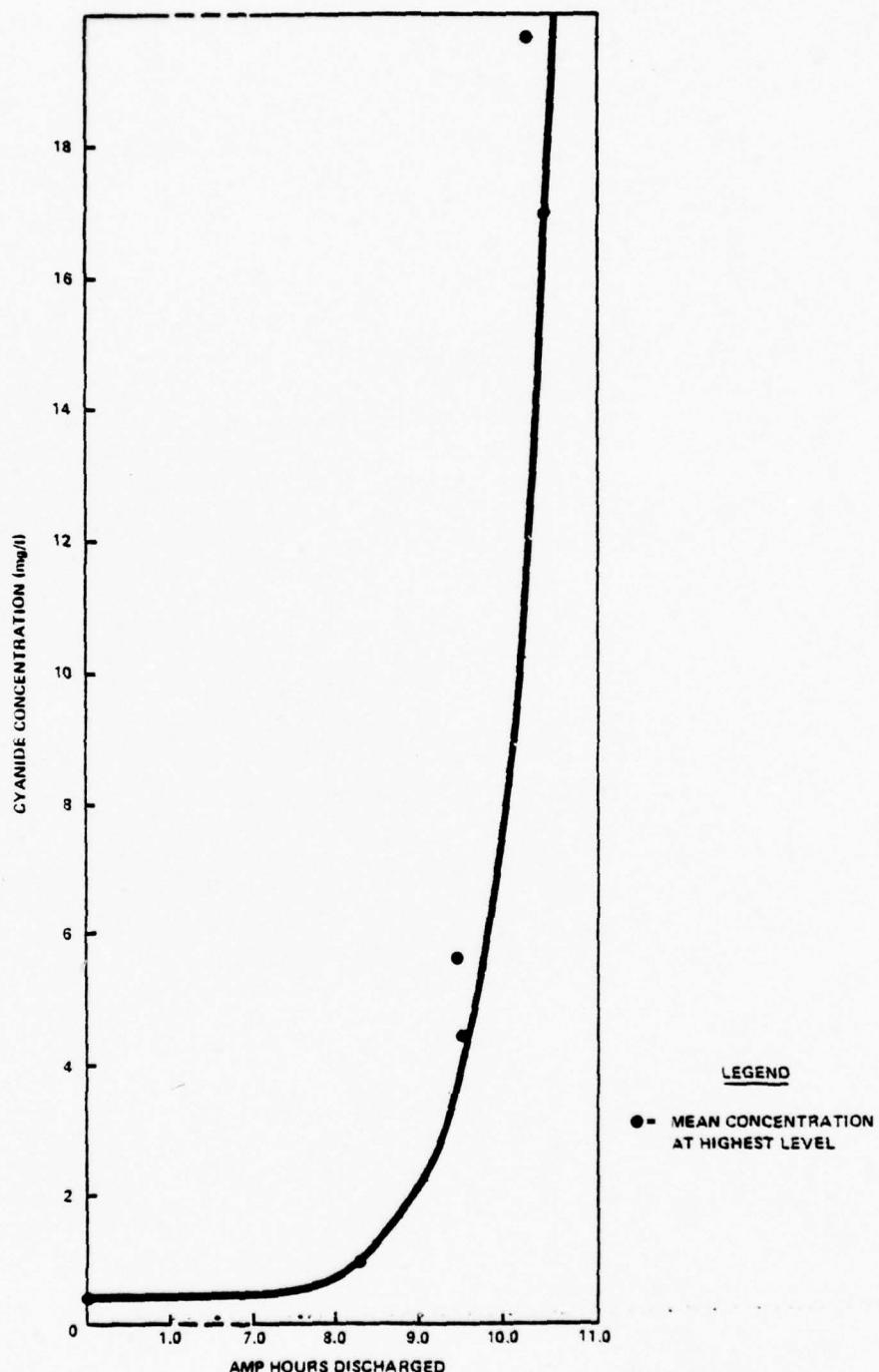


FIGURE 7 CYANIDE CONCENTRATION OF STANDARD LITHIUM CELLS VERSUS AMP HOURS DISCHARGED

Modified lithium cells discharged to the 1.7 and negative voltage levels were far more acidic than similarly discharged standard cells. These data appear to indicate that cells which contain significant levels of SO₂ are releasing it into solution in the form of sulfurous acid. As noted, these are the cells which either have not been discharged or, in the case of the modified cells, contained excess amounts of SO₂. Higher pH values in discharged standard lithium cells may also have been due to the formation of lithium hydroxide (a strong base) during discharge.

Statistical Evaluation of Results

The characterization of the levels of cyanide produced within standard and modified lithium cells was conducted by simultaneously testing ten cells under similar discharge conditions. Some variation in both the physical discharge characteristics and chemical reactions apparently occurred during discharge (see Tables B-11 through B-14).

Cyanide analyses performed on standard cells at six levels of discharge are summarized in Table 5. The greatest variations between cells occur at the 2.4 and 1.7 volt levels. Standard deviations are 66 and 61 percent of the respective mean cyanide concentrations in these cells. Comparison of analyses from samples collected 24 and 48 hours after cells were opened generally reveal no change in dissolution of cyanide. Statistical analysis indicates that only variations for cells discharged to negative voltage are significant at the 95 percent confidence level.

Evaluation of data on the actual amp-hours used to discharge lithium cells also points out that variations exist in the physical discharge characteristics of cells. Data presented in Table 5 show the greatest variations between cells occurred at the 2.4, 2.0, and 1.7 volt levels. Similar fluctuations in cyanide concentration and amp hours were also observed in the modified lithium cells tested (see Table 5).

Statistical analysis of the variations between different voltage levels was also conducted. This evaluation included examination of both differences in cyanide concentration and amp-hours of usage. Significant

TABLE 5. STATISTICAL SUMMARY OF DISCHARGE TESTING AND LABORATORY ANALYSIS RESULTS

<u>DISCHARGE LEVEL (Volts)</u>	<u>DISCHARGE LEVEL (Amp Hours)</u>	<u>CYANIDE CONCENTRATION (mg/l)</u>		
<u>Standard Cells</u>	<u>Average</u>	<u>Standard Deviation</u>	<u>Average</u>	<u>Standard Deviation</u>
2.84 (no discharge)	0.00	0.00	0.32	0.13
2.40	8.29	0.49	0.92	0.61
2.00	9.50	0.29	5.60	2.16
1.70	9.55	0.32	4.40	2.68
0.10	10.55	0.22	16.90	6.34
-3.88 (Average)	10.27	0.06	19.56	4.89
 <u>Modified Cells</u>				
1.70	7.25	0.43	0.032	0.008
-3.84 (Average)	8.44	0.00	0.026	0.003

differences occurred in the mean cyanide concentration of standard lithium cells discharged at the 2.84 and 2.40 volt levels, the 2.40 and 2.00 levels and the 1.70 and 0.10 volt levels. Standard t-test analysis showed no significant difference in the variations between the means of the 2.00 and 1.70 volt levels and in the 0.10 and negative voltage cyanide values at the 95 percent confidence level. Results are included in Table 6. Similar results were obtained from t-test analysis of variations in amp-hours of usage.

TABLE 6. STATISTICAL SUMMARY OF LABORATORY ANALYSIS RESULTS

<u>Discharge Level (Volts)</u>	<u>Average Cyanide Concentration (mg/l)</u>	<u>Variance</u>	<u>t-Value</u>	<u>Difference</u>
2.84 (no discharge)	0.32	0.0	2.2981	Significant
2.40	0.92	0.61	6.0648	Significant
2.00	5.60	4.16	1.0070	Not Significant
1.70	4.40	7.20	5.1556	Significant
0.10	16.90	40.20	0.9957	Not Significant
-3.88 (Average)	19.56	21.49		

Statistical analysis of both laboratory data and discharge testing indicates that when the period of discharge is increased (lower cell voltage and increased amp-hours of use), an increased production of cyanide occurs within the standard lithium cell. (See Tables 6 and 7). Amp-hours of discharge and voltage decrease from a cell seem to correlate with the increase in soluble cyanide produced by the cell. Neither, however, can be considered as an accurate index of the potential cyanide contained in a discharged standard cell.

TABLE 7. STATISTICAL SUMMARY OF DISCHARGE TESTING RESULTS

<u>Discharge Level (Volts)</u>	<u>Average Amp</u>		<u>Variance</u>	<u>t-Value</u>	<u>Difference</u>
	<u>Hours</u>				
2.84 (no discharge)	0.00		0.00	54.183	Significant
2.40	8.29		0.21	7.1176	Significant
2.00	9.50		0.07	0.1815	Not Significant
1.70	9.55		0.09	3.8639	Significant
0.10	10.55		0.04	1.5761	Not Significant
-3.88 (Average)	10.27		0.003		

C. Leachate Column Tests

As a further evaluation of the environmental impact of the land disposal of lithium batteries, it was important to determine whether different soil types would affect the concentrations of standard cell constituents in water percolating through the soil. An assessment of the mobility and transport of toxic or potentially hazardous materials and the degree to which they were absorbed by soils was made. This consisted of a comparison between the concentrations of cell constituents in leachate and the levels solubilized in distilled water testing (Section IIB).

Three different soil types were selected for this evaluation. They included sandy loam (Lakeland), silty loam (Mattapeake) and silty clay (Hagerstown) soils. Three leachate columns were prepared with each soil, one containing two fully discharged standard lithium cells, a second containing two live standard cells and a third serving as a test control column. A detailed description of the materials and procedures utilized to pack these columns and collect the leachate samples was presented in the Phase I Report.¹² Analysis of leachate samples included characterization of lithium, sulfite and cyanide concentrations for sandy loam soil and monitoring of pH and conductivity levels. Only pH, conductivity and cyanide analyses were performed on silty loam and silty clay soil leachates. Figure 8 shows actual laboratory leachate testing in progress.

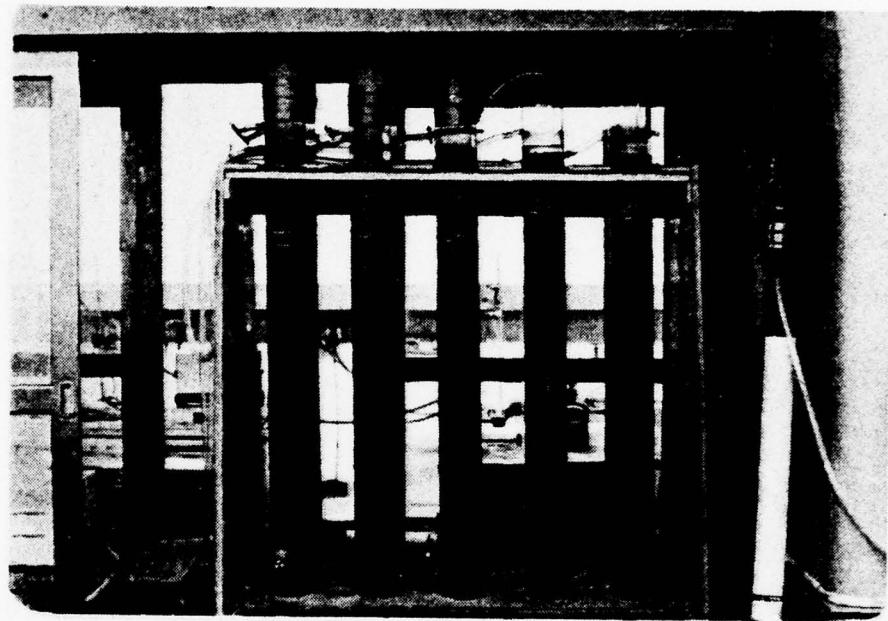


FIGURE 8 LEACHATE TESTING OF DISCHARGED STANDARD LITHIUM CELLS IN VARIOUS SOIL TYPES

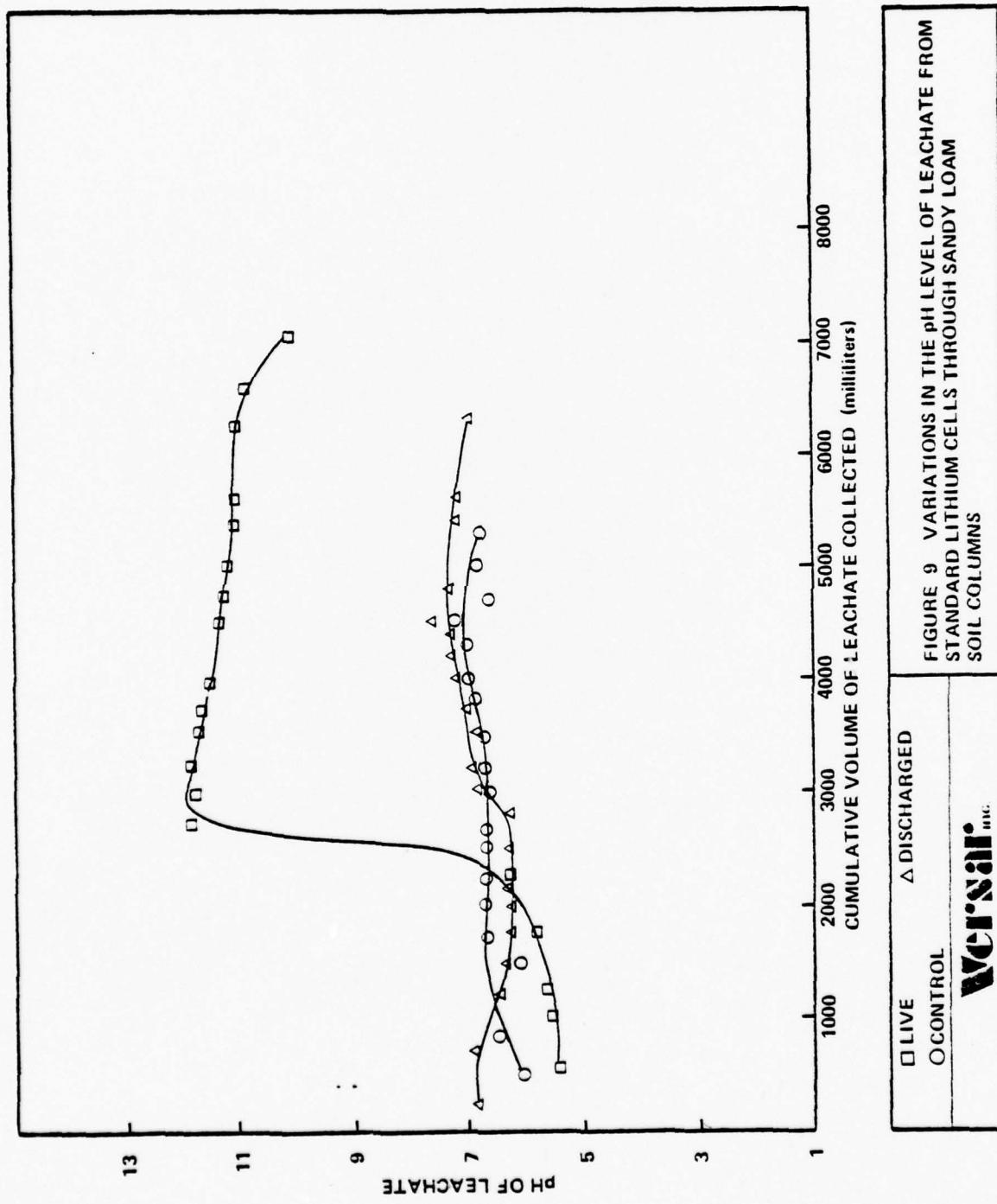
Results of Lakeland Sandy Loam Tests

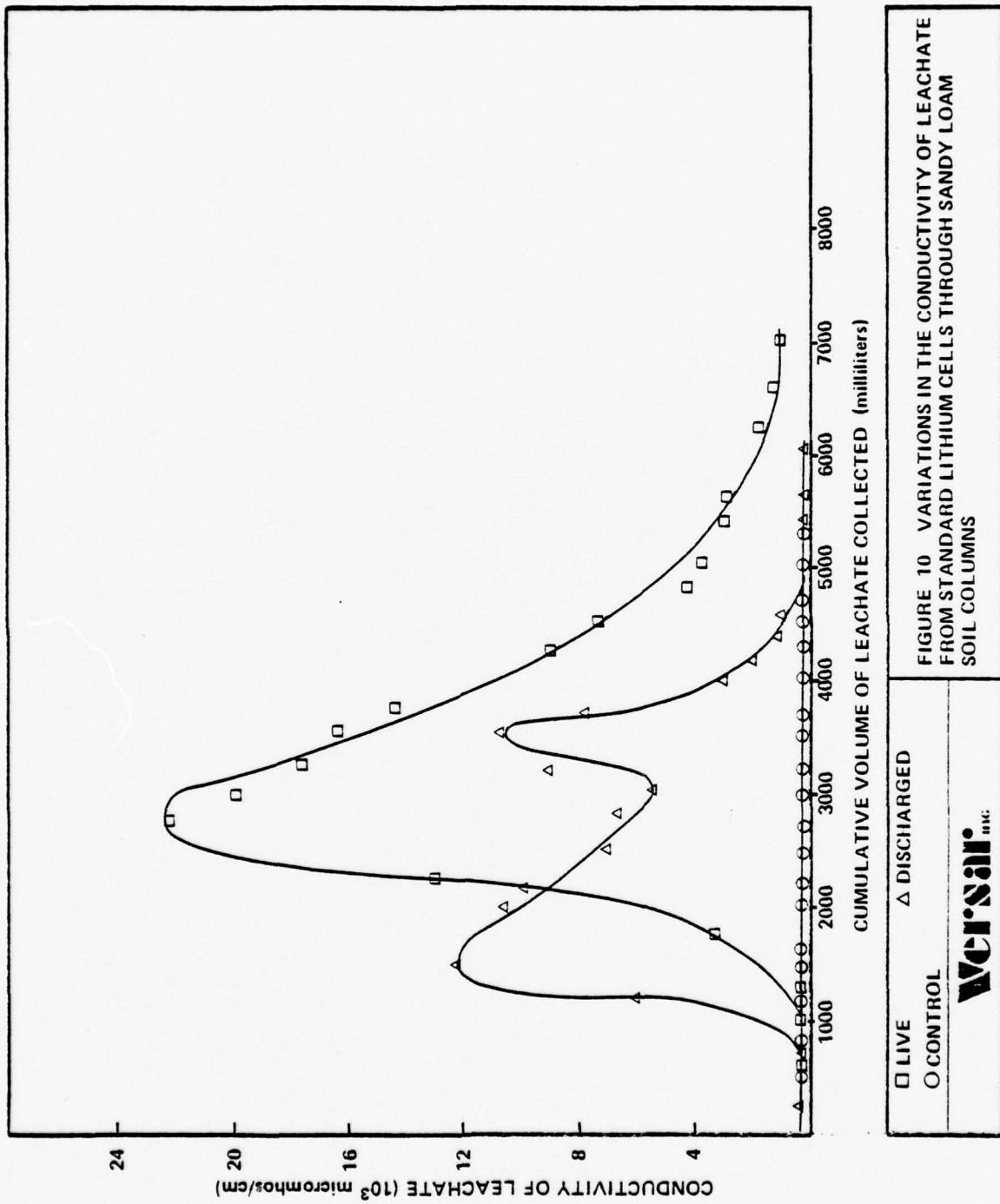
The monitoring of pH and conductivity levels in leachate from sandy loam soil served as an index of the migration of lithium cell components through the column. It also provided some indication if soluble lithium waste components had finished migrating through the soil. When pH and conductivity levels of leachate from columns containing cells compared with control leachate, migration was considered complete. Figures 9 and 10 illustrate the points at which maximum leaching of lithium cell components occurred.

Migration of the chemical constituents from both live and discharged standard cells, as shown in Figures 11 and 12, indicated that lithium, sulfite and cyanide were transported in the same portion of leachate. The mobility of these components through the sandy loam column appeared to be quite similar. A long steady migration through the soil column apparently occurs, with significant amounts of the cell contained in 3,000 ml of the leachate collected.

The maximum concentrations of sulfite (11,100 mg/l) in leachate from discharged cells, occurred after 1,670 ml of leachate had been collected (passed through the column), seven days following initiation of the test (See Phase I Report Table C-5). In comparison, a maximum sulfite concentration of 11,400 mg/l occurred after 2,305 ml of leachate had been collected from the live cell column. This peak was reported six days after testing had begun (See Phase I Report Table C-5). Total soluble sulfite collected in leachate samples was 12.88 g per discharged cell and 8.37 g per live cell.

Lithium reached a maximum concentration of 2,035 mg/l in discharge cell leachate through sandy loam. This peak occurred at the same time (in the same leachate sample) that maximum sulfite levels were recorded. In the column containing live cells, a maximum concentration of 3,035 mg/l of lithium was observed one day (500 ml of leachate) after the corresponding sulfite peak. The total amount of soluble lithium transported through sandy loam columns was 2.49 g per discharged cell and 2.97 g per live cell.





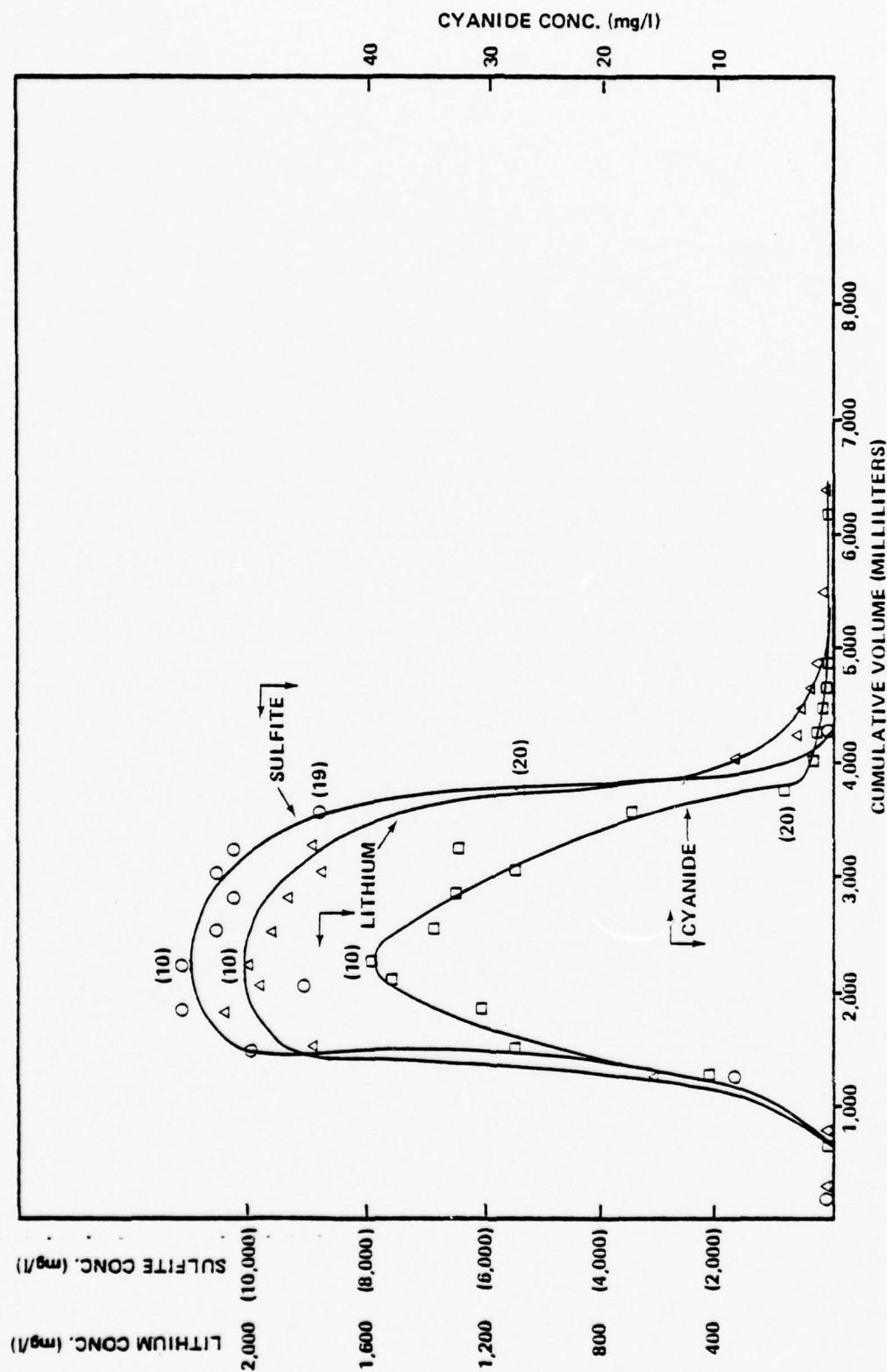


FIGURE 11 VARIATIONS IN LITHIUM, SULFITE AND CYANIDE CONCENTRATIONS IN LEACHATE FROM DISCHARGED STANDARD LITHIUM CELLS THROUGH A SANDY LOAM SOIL COLUMN

□ CYANIDE
 △ LITHIUM
 ○ SULFITE
Ver-Sal[®] Inc.

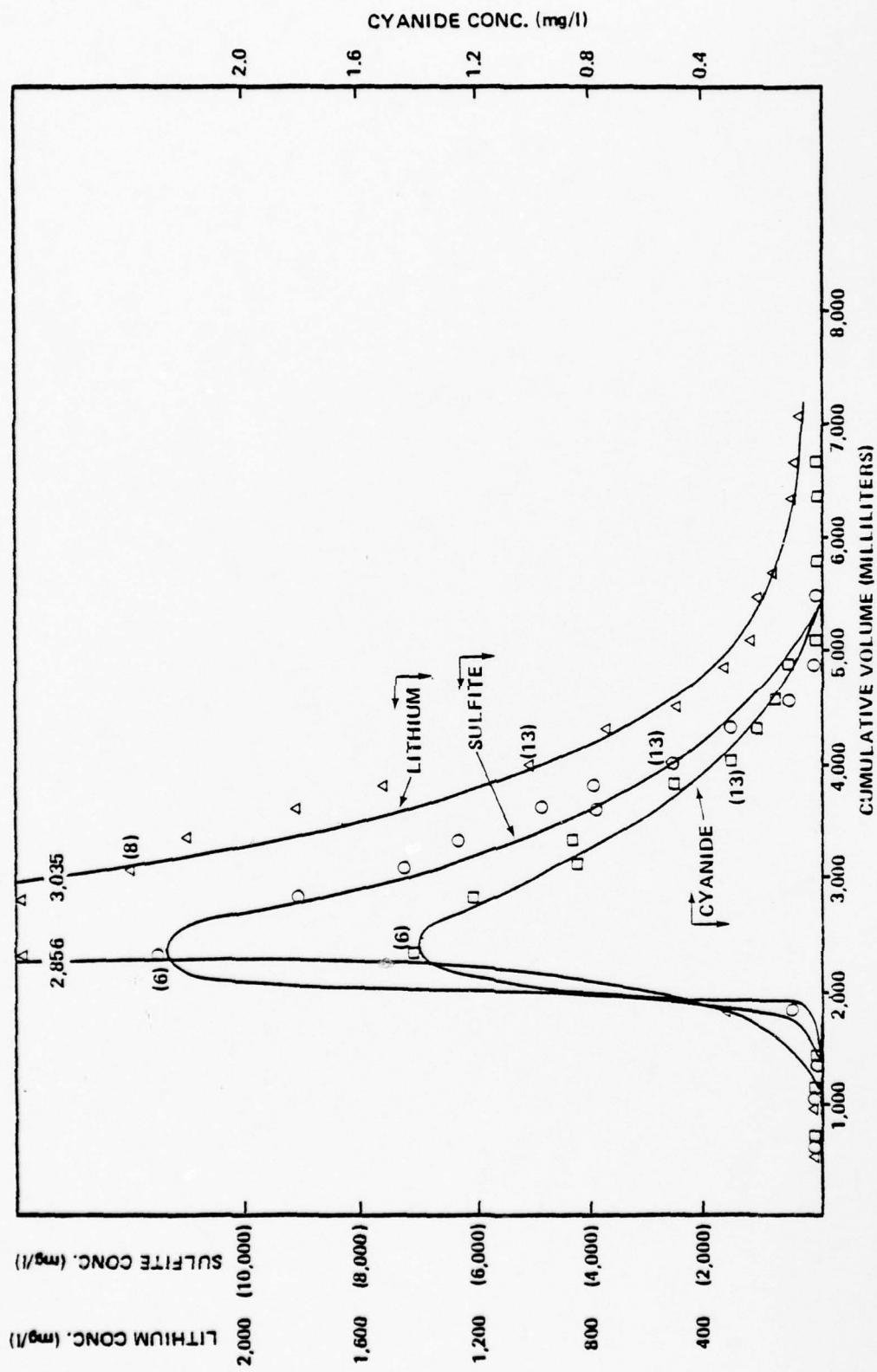


FIGURE 12 VARIATIONS IN LITHIUM, SULFITE AND CYANIDE CONCENTRATIONS IN LEACHATE FROM LIVE STANDARD LITHIUM CELLS THROUGH A SANDY LOAM SOIL COLUMN

Verall Inc.

These values indicate no significant difference in lithium transported through sandy loam from either discharged or live standard cells.

Cyanide concentration of leachate from discharged cells reached a maximum of 39.0 mg/l after ten days (2,220 ml), and decreased somewhat consistently to less than 1.0 mg/l after 24 days (4,525 ml). Live cell leachate cyanide concentrations reached a maximum of 1.40 mg/l after six days (2,305 ml), and decreased to less than 0.2 mg/l at 17 days (4,695 ml). Detailed results of leachate analyses are presented in Tables B-16 through B-18. Variations in cyanide concentration of leachate through sandy loam are also illustrated in Figure 13.

Leachate testing results indicate that 40.59 mg of soluble cyanide were transported from a discharged standard cell through the sandy loam column, and 1.16 mg from a live cell. Table 8 summarizes these cyanide data for discharged and live cells for all three soil types.

TABLE 8. SOLUBLE CYANIDE CONTAINED IN SOIL COLUMN LEACHATE TESTS

<u>Soil Type</u>	<u>Cell Condition</u>	<u>Cyanide in Leachate mg/cell</u>
Sandy Loam (Lakeland)	Live	1.16
	Discharged	40.59
Silty Loam (Mattapeake)	Live	<0.01
	Discharged	42.11
Silty Clay (Hagerstown)	Live	<0.01
	Discharged	33.49

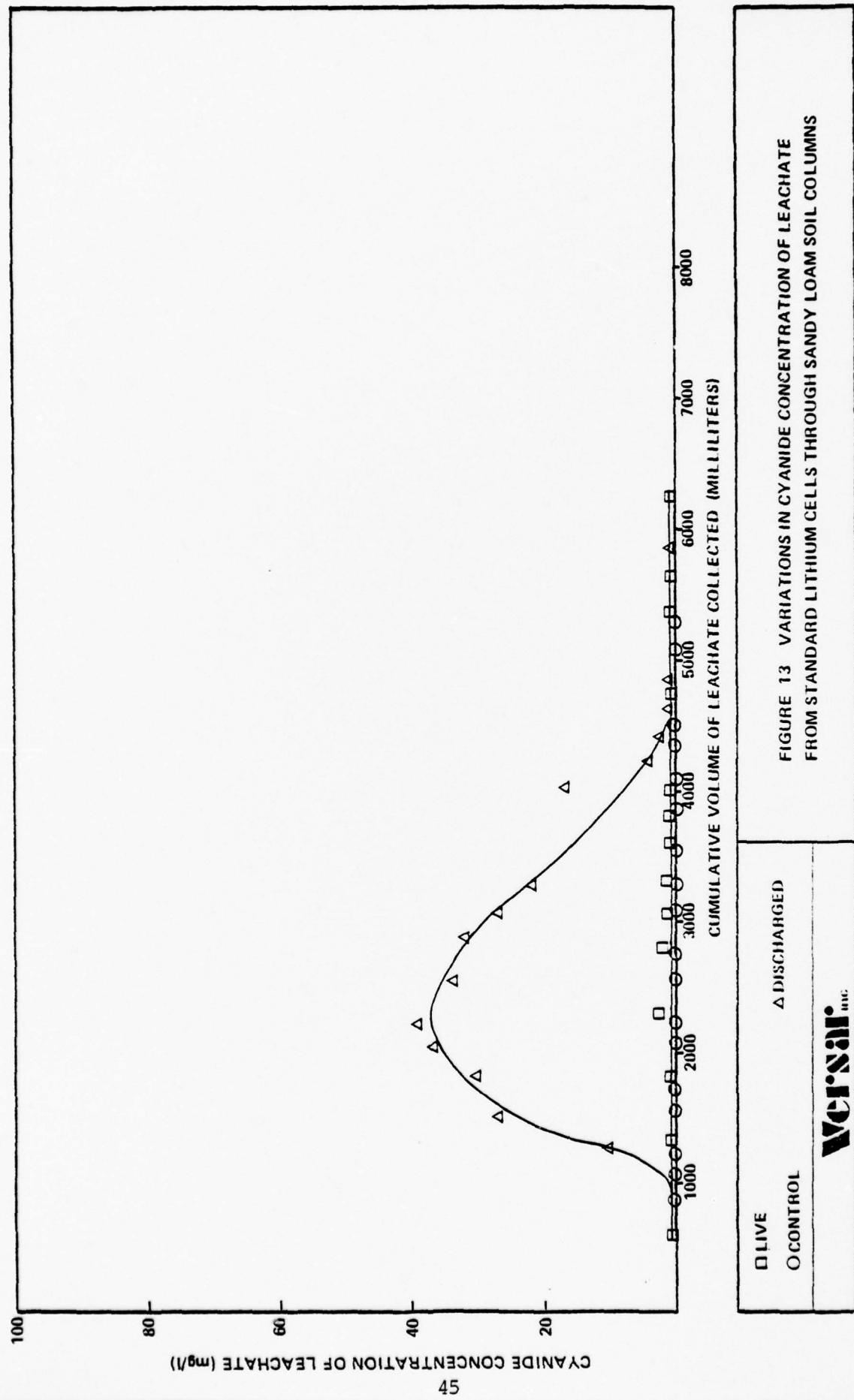


FIGURE 13 VARIATIONS IN CYANIDE CONCENTRATION OF LEACHATE FROM STANDARD LITHIUM CELLS THROUGH SANDY LOAM SOIL COLUMNS

DISCHARGED
LIVE
O CONTROL
VERSAT

Results of Mattapeake Silty Loam Tests

Results of pH, conductivity and cyanide analysis in leachate from silty loam soil indicate that migration of discharged standard lithium cell components was contained in a smaller portion of the leachate, and concentrated in more of a slug than observed in sandy loam (Lakeland) testing. Figures 14 through 16 show that peak concentrations in the leachate however, did not occur for all components of the cell at the same time. Cell components were concentrated in about 2,000 ml of the leachate collected.

Cyanide concentrations of leachate from discharged cells reached a maximum of 70 mg/l after 182 days (3175 ml). Levels of cyanide within the leachate had decreased to 3.25 mg/l at the conclusion of leachate testing (See Table B-19). Figure 17 illustrates the differences observed in migration rate of standard lithium cell components through sandy loam and silty loam soil. A total of 42.11 mg of soluble cyanide was transported from a discharged cell through the silty loam column. Less than 0.01 mg of cyanide was reported in leachate from live cells.

Results of Hagerstown Silty Clay Tests

Migration of discharged standard lithium cell components through silty clay (Hagerstown) seemed to follow more the pattern observed in silty loam than sandy loam soil. Figures 18 through 20 show that peak concentrations in the leachate occurred in a much smaller portion of the leachate collected; in a clearly defined slug. Only 1,300 ml of the leachate contained significant amounts of cell components.

Cyanide concentrations reached a maximum of 88.4 mg/l after 200 days (3,000 ml of collected leachate), and had decreased to 3.00 mg/l by the conclusion of leachate testing. (See Table B-22). A total of 33.49 mg of soluble cyanide was collected from a discharged cell leachate through silty clay. Less than 0.01 mg of cyanide was reported in leachate from live cells.

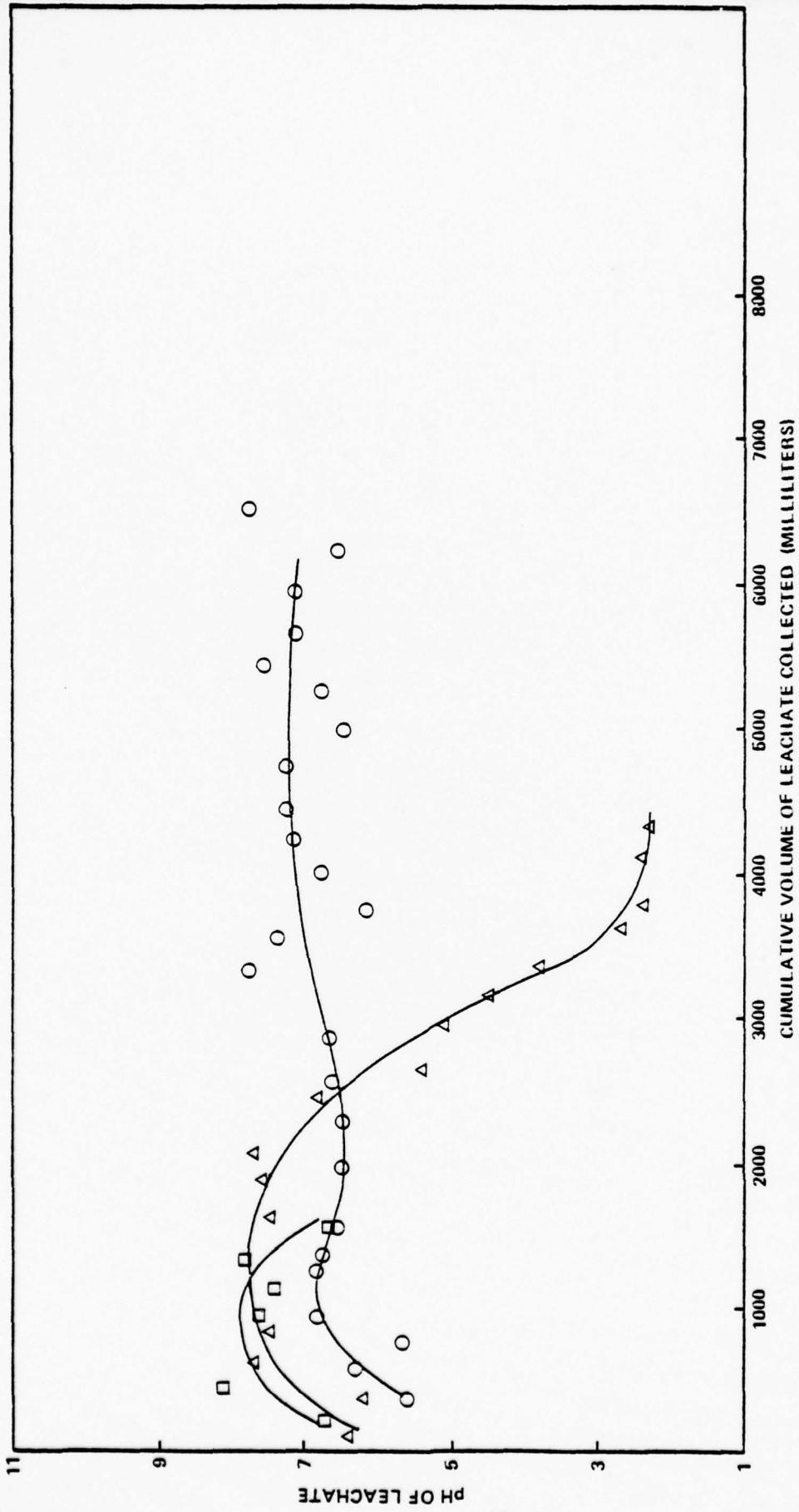


FIGURE 14 VARIATIONS IN THE pH LEVEL OF LEACHATE FROM STANDARD LITHIUM CELLS THROUGH SILTY LOAM SOIL COLUMNS

□ LIVE
○ CONTROL
△ DISCHARGED

Veri-Sail INC.

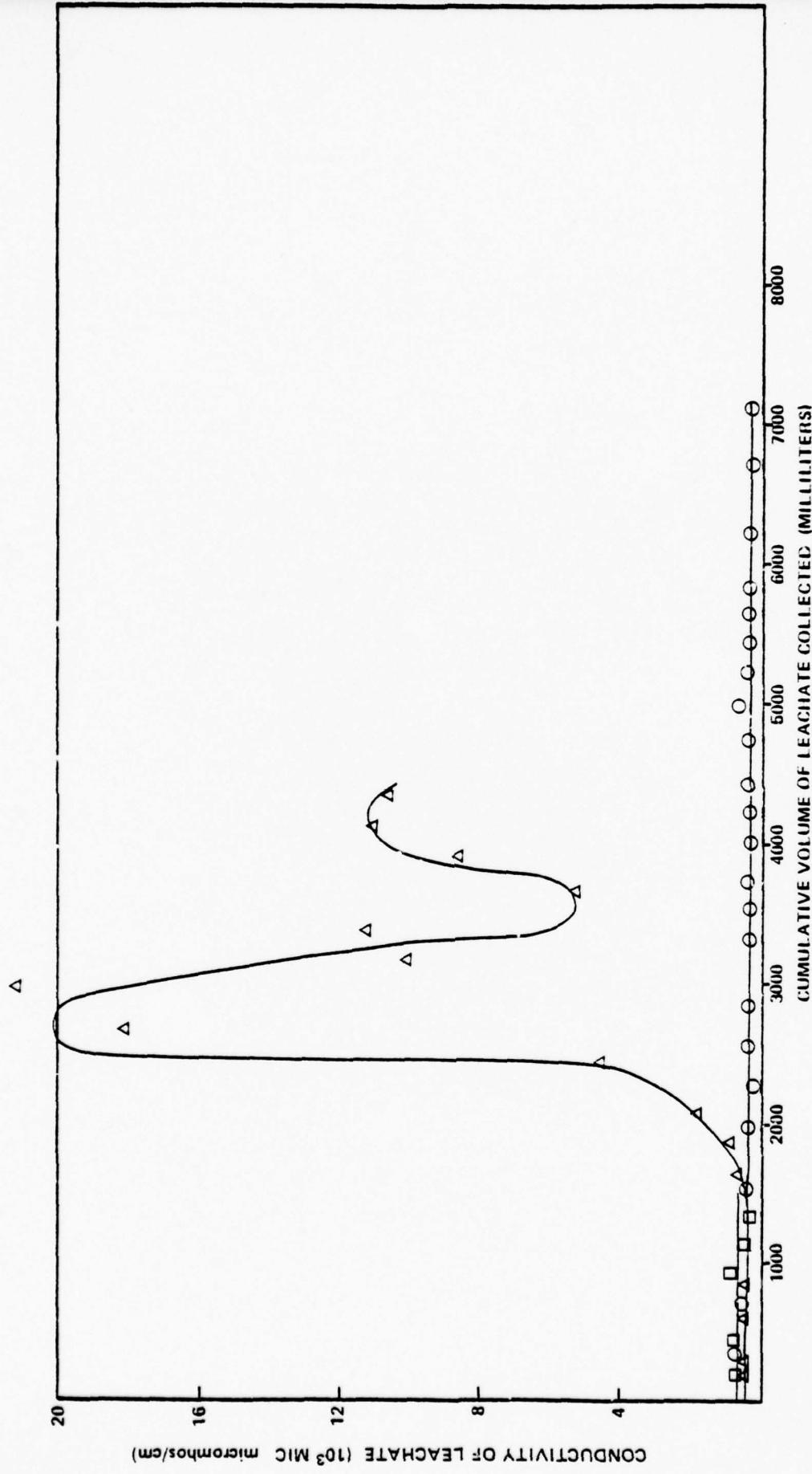


FIGURE 15 VARIATIONS IN THE CONDUCTIVITY OF LEACHATE FROM STANDARD LITHIUM CELLS THROUGH SILTY LOAM SOIL COLUMNS

Verhall inc.

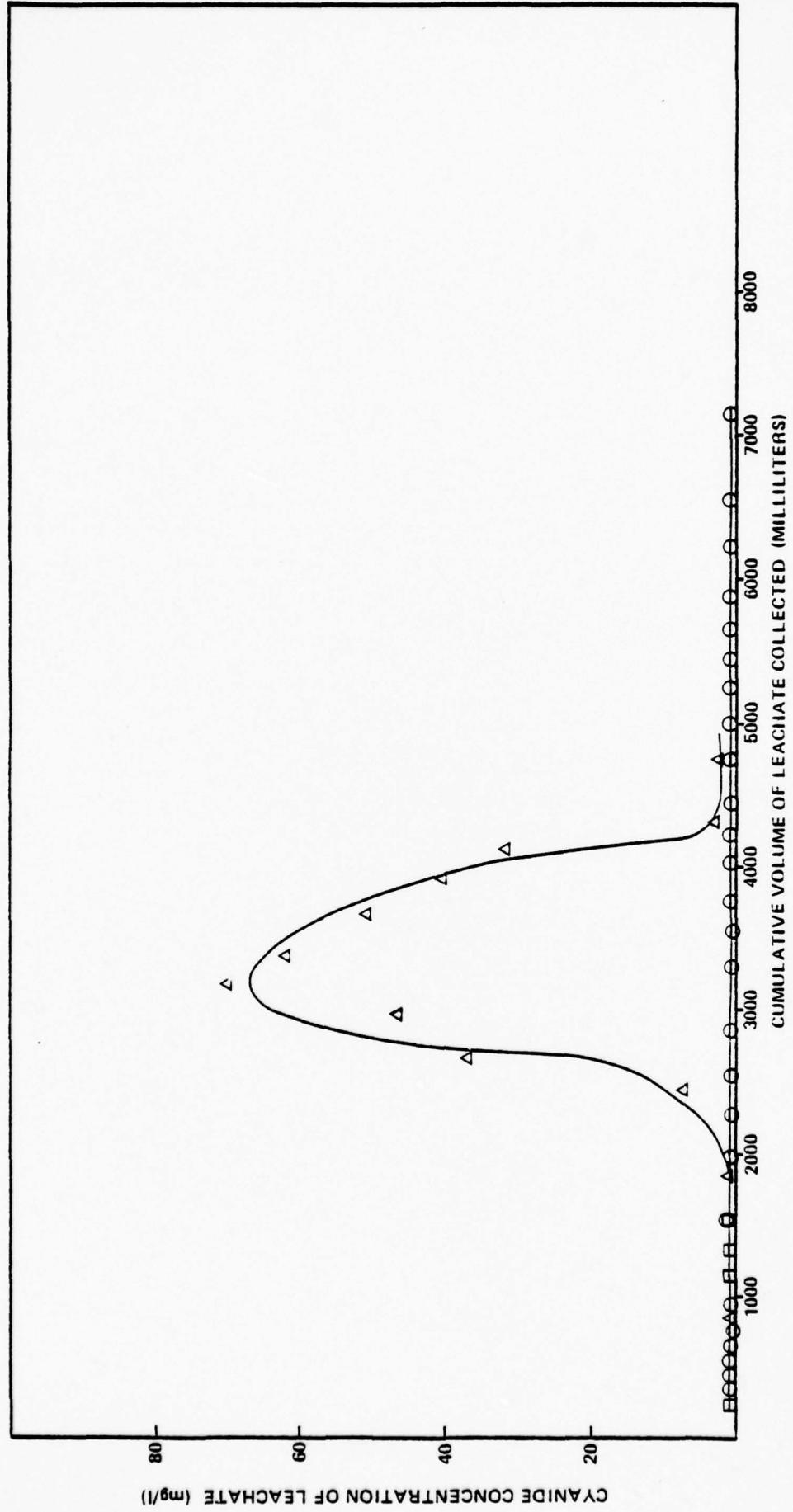
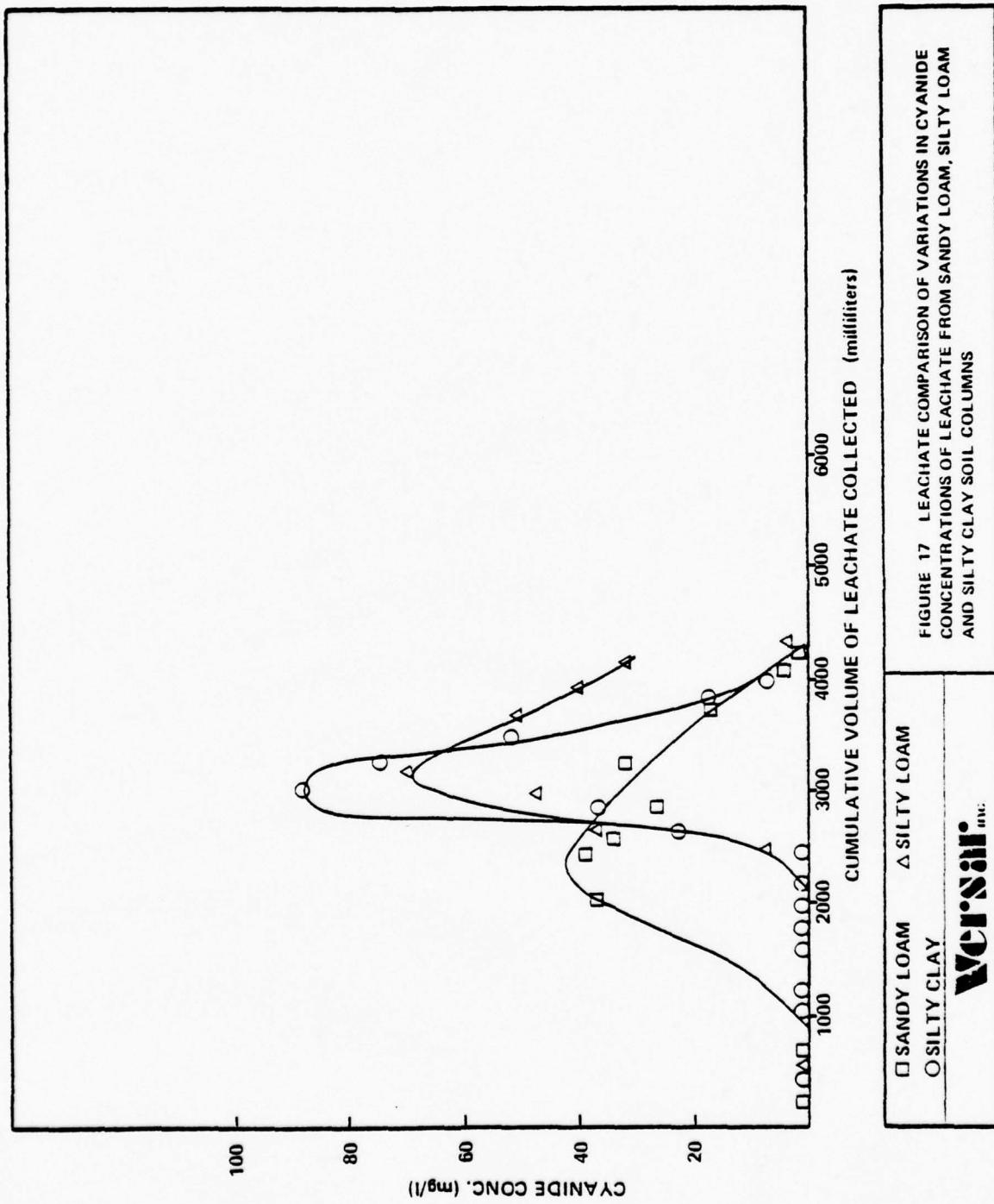


FIGURE 16 VARIATIONS IN CYANIDE CONCENTRATION OF LEACHATE FROM STANDARD LITHIUM CELLS THROUGH SILTY LOAM SOIL COLUMNS

□ LIVE
○ CONTROL
△ DISCHARGED

WERNAL INC.



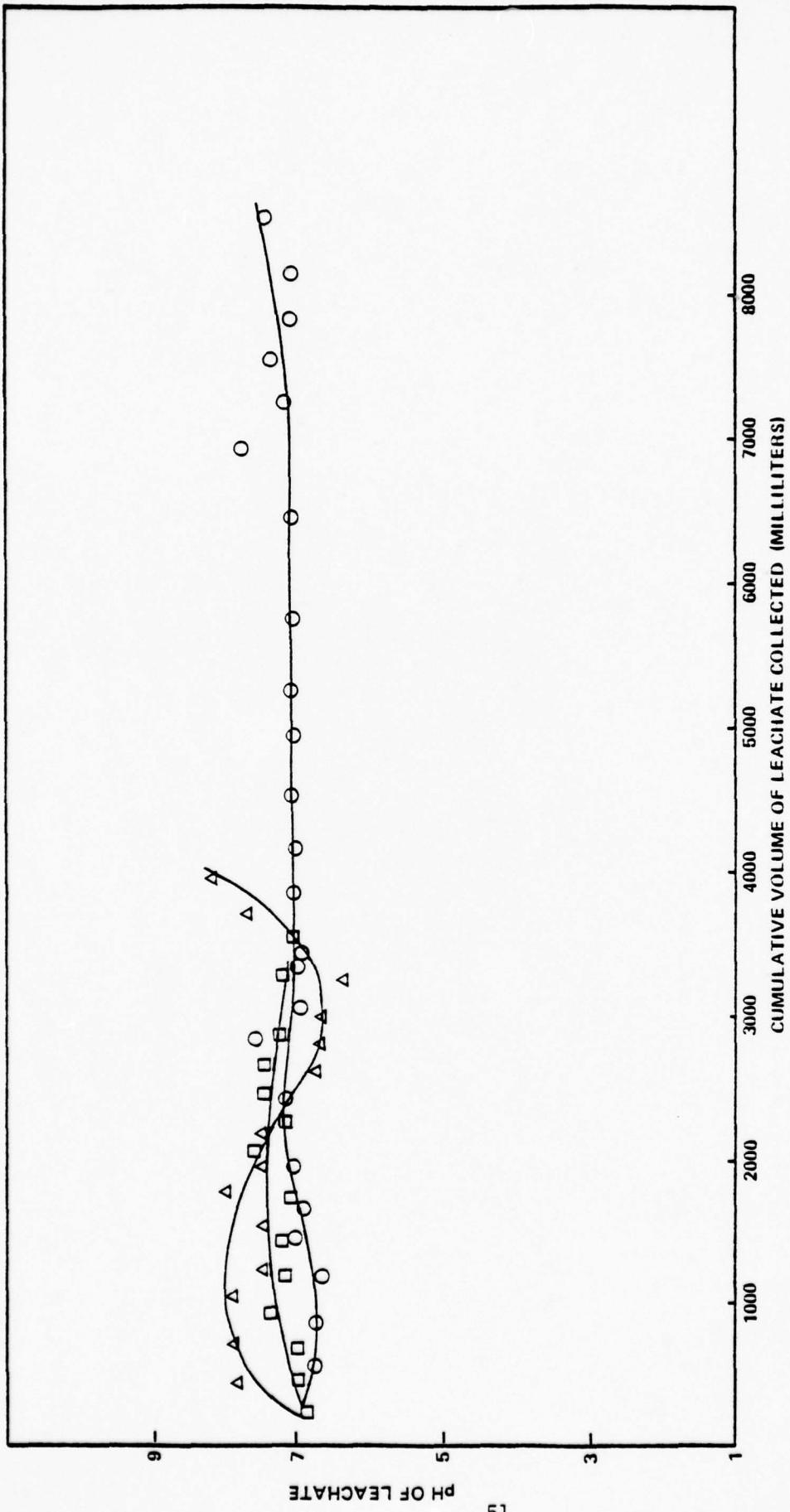


FIGURE 18 VARIATIONS IN THE pH LEVEL OF LEACHATE FROM STANDARD LITHIUM CELLS THROUGH SILTY CLAY SOIL COLUMNS

OLIVE
O CONTROL
△ DISCHARGED

Ver-Sail INC.

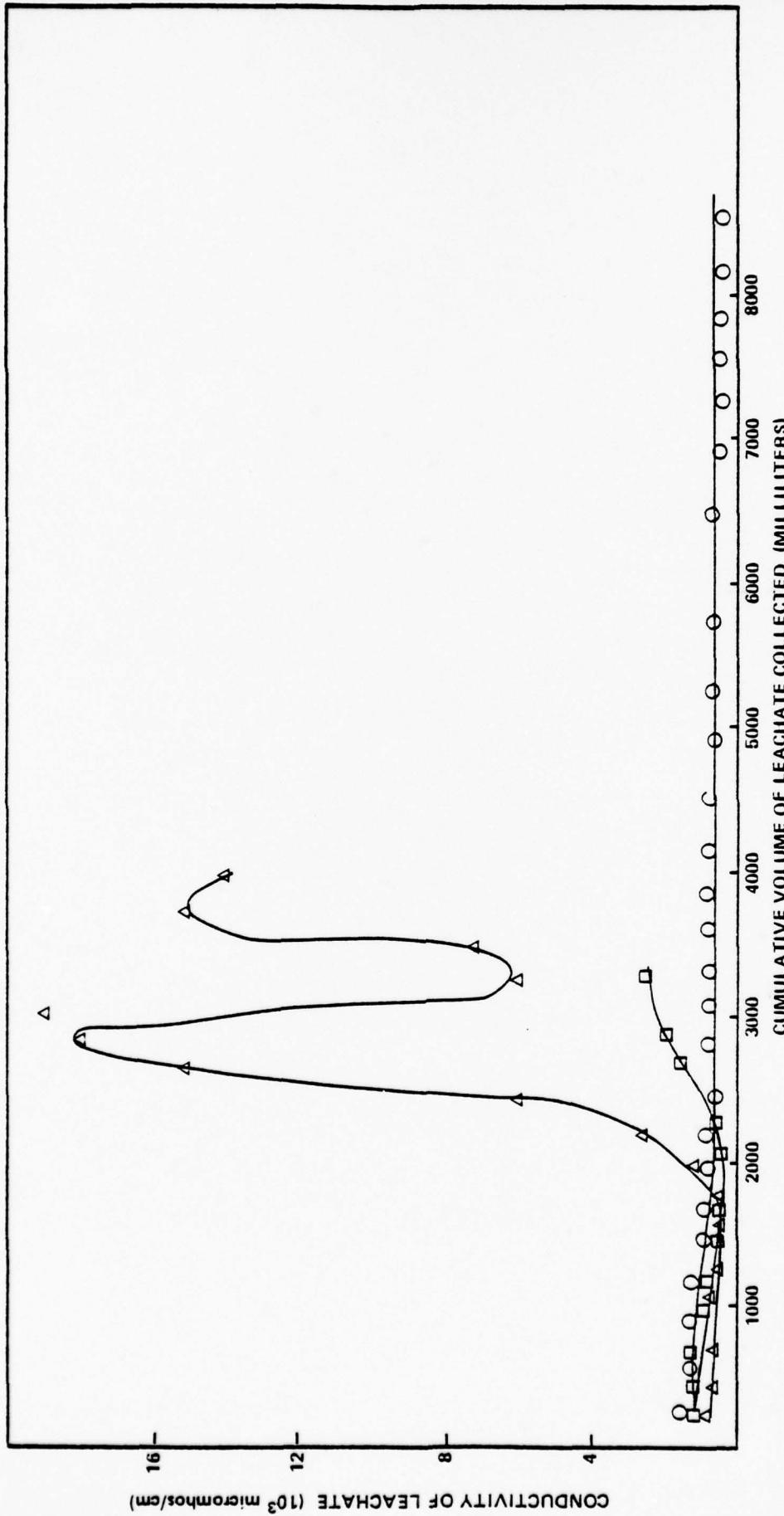


FIGURE 19 VARIATIONS IN THE CONDUCTIVITY OF LEACHATE FROM STANDARD LITHIUM CELLS THROUGH SILTY CLAY SOIL COLUMNS

Veri-Wall[®] Inc.

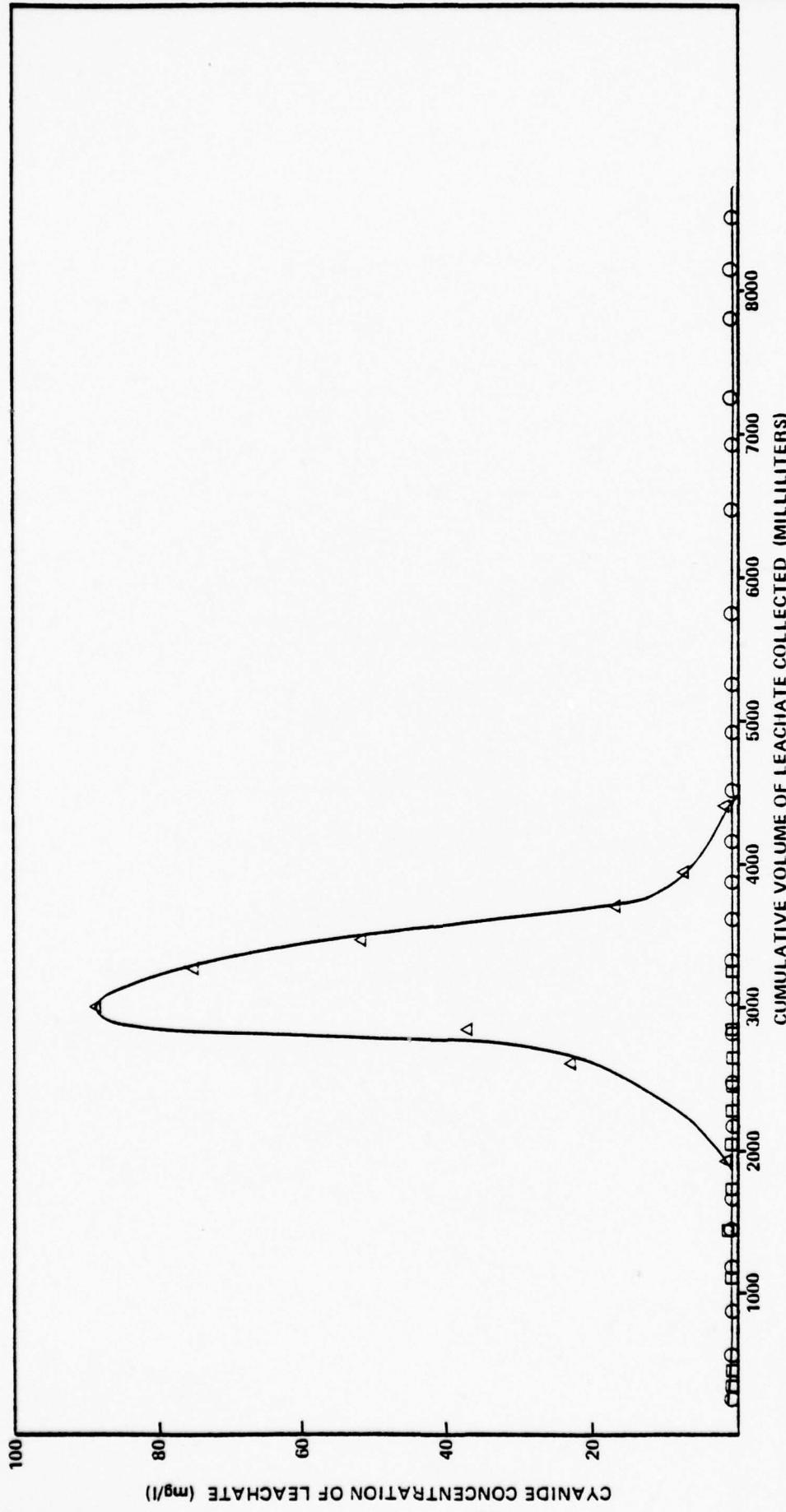


FIGURE 20 VARIATIONS IN CYANIDE CONCENTRATION OF LEACHATE
FROM STANDARD LITHIUM CELLS THROUGH SILTY CLAY SOIL COLUMNS

□ LIVE
○ CONTROL
△ DISCHARGED
Verallu^{inc}

Evaluation of Leachate Transport Through Leachate Columns

Characterization of land disposal environmental impacts of lithium batteries required an assessment of the mobility and transport of toxic or potential hazardous cell components and the degree to which they were adsorbed in different soils. Finally, it was also important to determine approximately what the concentration of these cell components were in the leachate which potentially could be introduced into a groundwater supply.

Data on the mobility of the cell components through leachate columns indicate that the migration rate was faster through sandy loam (Lakeland). Figure II-11 shows that maximum lithium, sulfite and cyanide concentrations occurred in a sample after 2,540 ml (40 percent) of the total leachate was collected. This sample contained approximately 13 percent of the cyanide recovered in the leachate through sandy loam. Results of leachate testing of discharged standard cells through silty loam (Mattapeake) revealed that migration of cell components was slower. Maximum cyanide concentrations were recorded after 3,175 ml (66 percent) of the total leachate was collected. This sample, as was noted above, represented more of a leachate slug, with almost 17 percent of the cyanide recovered appearing in this sample. Silty clay leachate samples were even more concentrated. Maximum cyanide levels were observed after 3,300 ml (88 percent) of the total leachate was collected. This sample contained 28 percent of the soluble cyanide that leached through the silty clay column. Figure 21 illustrates the comparative migration rates of cyanide waste through these three soil types.

Determining the level of adsorption of the lithium cell constituents in different soil types proved to be quite difficult. Conclusions are limited because of the high variability in cyanide concentrations observed in discharged standard cells. The difference between the 33.49 mg per cell collected from silty clay leachate and the 40.59 mg per cell from sandy loam cannot be considered as the amount adsorbed by silty clay. Variations of this magnitude were also seen in simultaneously discharged cells placed in an aqueous media (Section IIB). Results of live cell leachate testing,

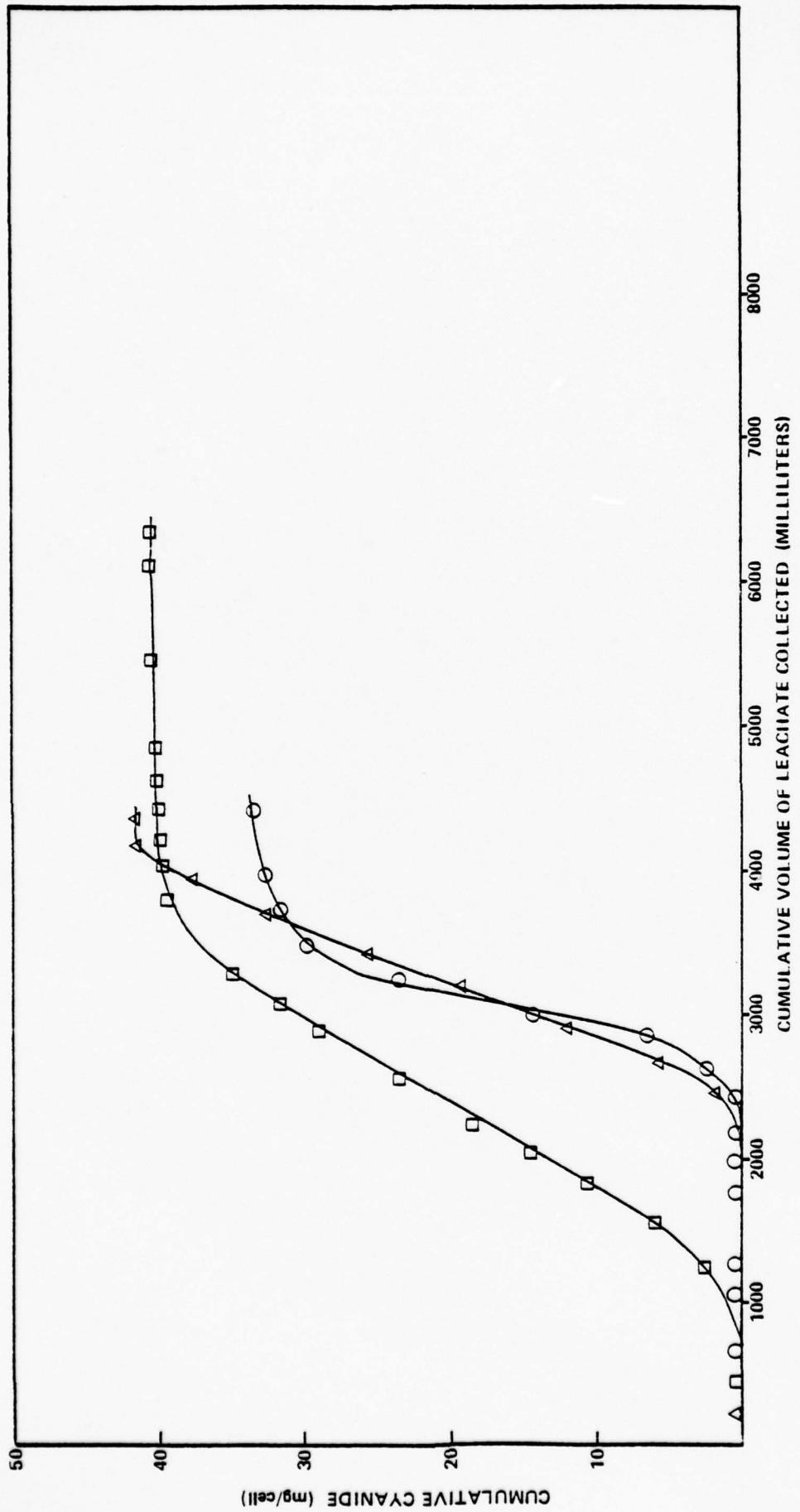


FIGURE 21 CUMULATIVE CYANIDE IN LEACHATE FROM SOIL COLUMNS
CONTAINING TWO DISCHARGED STANDARD LITHIUM CELLS

□ SANDY LOAM △ SILTY LOAM
○ SILTY CLAY

Vernall inc.

however, indicate that some adsorption of cyanide may have taken place in silty loam and silty clay columns. Leachate collected from live cells through the sandy loam included 1.16 mg per cell of cyanide. Both the silty loam and silty clay leachate contained less than 0.01 mg per cell (See Table 8). The analysis of ten live standard cells during discharging testing never included a cell containing less than 0.20 mg per cell of soluble cyanide, indicating that some adsorption may have occurred.

In evaluation of the leachate produced from discharged standard lithium cells it is important to realize that cyanide levels from all soil columns far exceeded the 0.2 mg/l cyanide standard established for freshwater (drinking supply). The environmental impact that these leachates would have, and the extent to which they influence actual disposal density considerations, is discussed in the following section.

D. Assessment of General Landfill Disposal of Lithium Batteries

A leachate model was developed to evaluate how the laboratory results on the level of cyanide (soluble within a lithium cell and possibly contained in leachate), influence disposal considerations. The model attempts to indicate or predict the number of cells which could be disposed of per volume of landfill to minimize the environmental consequences of the lithium battery. However, this model is only able to estimate the average leachate cyanide concentration produced from disposal of cells. To calculate actual density estimates the model would need to include information on soil types, porosity, diffusion rates of cell constituents and site specific considerations. In addition, some estimates on the durability of cells during disposal and the period of time necessary for cell constituents to escape from the lithium cell casing would need to be included in the model. For example, all cells from a battery or group of batteries will not open at the same time following disposal. Research indicates that when a cell does open, it often begins as a pin hole and gradually enlarges. Cells opened during this program were stabilized in liquid nitrogen and then sawed completely in half exposing all soluble constituents, rather than allowing their possible gradual introduction. No laboratory data were available to confirm the differences which result from the two opening techniques.

1. Development of a General Case Density Guideline for Disposal of the Lithium Battery.

Development of a general case guideline for disposal of the lithium battery was requested by ECOM officials so that they could evaluate the feasibility of using these batteries in various operational situations. Specifically, ECOM was interested in estimating the number of discharged lithium cells which could be disposed of with solid waste (paper, glass, metal, etc.) generated on a field maneuver, for example, without adversely effecting the local environment. In this situation, lithium cells would be disposed of with this solid waste using general collection and sanitary landfill disposal methods. By knowing the volume of solid wastes generated ECOM hoped to establish a general disposal density guideline for lithium cells.

It is expected that through development of this guideline the U.S. Army could predict what the environmental impact of limited disposal of lithium batteries would be. Based on this guideline an impact statement could eventually be submitted to Federal and State regulatory agencies. It has been Versar's experience, in dealing with Federal and State agencies, that the consideration of density data for potential contaminants is not sufficient as rationale for disposal considerations. An attempt to control the disposal density of these cells and thus affect the potentially leachable cyanide does not appear to be a workable disposal alternative at present. There is no absolute guarantee that concentrated cell constituent leachate will not be discharged directly into a groundwater supply. Thus it would be necessary to perform on-site assessment of actual land disposal. This would include monitoring of landfill leachate and groundwater in the vicinity of the disposal site.

Description of the Leachate Model

To evaluate the environmental feasibility of the disposal of lithium batteries, a disposal density model for sanitary landfills has been developed. This model assumes that all leachate from rainfall becomes equally dispersed throughout a recently added layer of landfill, containing a lithium cell or cells, until that portion of the fill reaches field capacity (the saturation point). After saturation is achieved, any additional

precipitation will cause the leachate (potentially containing lithium cell components) from this layer of fill to follow a vertical migration through the landfill. The model also assumes that the cell constituents are uniformly dispersed in the leachate volume. The leachate cyanide concentration is characterized at the point it infiltrates the soil zone below the landfill, prior to its introduction to an aquifer, as if a monitoring well had been placed in the landfill and the depth of well just exceeded the depth of the landfill.

The model assumes a quantity of cyanide per cell available for release to the environment, based upon experimental discharge testing analysis. The model also assumes a volume of water necessary to provide a saturated condition for that portion of the landfill (containing compacted solid waste and soil) per unit volume of fill material. Salvato et al., in their studies of groundwater pollution from subsurface excavations, indicated that 41.1 liters of water per cubic meter of compacted solid waste would be required to reach this saturation point in a normal landfill.¹³ From these assumptions, an estimate of compacted solid waste volume in cubic meters can be calculated which would produce a cyanide concentration of 0.2 mg/l or less (designated EPA drinking water standard) in the leachate.

To convert these volume estimates to density figures that are more applicable to daily disposal practices utilized by the U.S. Army, ECOM provided data on the composition of solid waste generated at U.S. Army locations. These data, as presented in Table 9, were comprised of somewhat a normal composition of solid waste, much like that typically found in a sanitary landfill.¹⁴ Since no actual data was available on the volume density of this waste an average value was used. A recent survey of municipal landfills in various regions of the U.S. including fills of different depths, sizes and soil compositions indicated that 100 pounds per cubic meter (lb/m^3) was an average compacted volume density.¹⁴ This value is utilized in the model.

The general case model can then be used to calculate the volume of solid waste to be disposed of per lithium cell to produce a leachate less than 0.2 mg/l cyanide through the landfill. From this figure a disposal density conversion to cells per pounds of solid waste can be computed. By including ECOM's estimate of solid waste generated per person per day of five (5) pounds, the model can be utilized to determine the number of cells which can be disposed of with each person's individual waste each

TABLE 9. ESTIMATED COMPOSITION OF SOLID WASTE GENERATED
AT U.S. ARMY LOCATION¹⁵

<u>SOLID WASTE TYPE</u>	<u>PERCENT OF TOTAL SOLID WASTE</u>
Paper and Paper Products	55.7
Glass	7.4
Ferrous Metals	9.2
Aluminum	0.5
Other Metals	0.7
Food Waste	5.3
Plastics	1.5
Rubber	2.4
Textiles	2.9
Wood, Leaves, Branches, etc.	14.4

day (cells/person/day). This is the disposal density calculation which ECOM feels is most applicable for their evaluation of environmental assessment. An example of the model as used in this manner, applying the laboratory test data from Table 2, is illustrated below.

Application of Model Using Lithium Battery Laboratory Test Data

To evaluate the "worst case" consequences of lithium cell disposal the highest average soluble cyanide concentration reported for a discharge level was applied to the model. This maximum value of 97.8 mg per cell was observed in standard cells discharged to a negative voltage level. Thus, to insure that possible leachate produced from this cell contains an average of less than 0.2 mg/l cyanide would require;

$$\frac{97.8 \text{ mg/cell}}{0.2 \text{ mg/l}} = 489 \text{ liters}$$

or that cyanide formulated in one cell be diluted with 489 liters of water prior to its infiltration of the soil below the landfill. This means that the volume density needed for disposal of one cell must be large enough to guarantee that its saturation point (where additional liquid input will result in leachate) is greater than or equal to 489 liters. A calculation shows that this would require an 11.9 cubic meter portion of a landfill, since each cubic meter holds 41.1 liters of water before leaching takes place. Thus,

$$\frac{489 \text{ l (needed to dilute one cell to } 0.2 \text{ mg/l CN}^-)}{41.1/1 \text{ (needed to saturate one cubic meter of fill)}}$$

or, 11.9 m^3 of solid waste per cell would be necessary.

Since one cubic meter of fill represents 100 pounds of solid waste, then 1,190 ($11.9 \text{ m}^3 \times 100 \text{ lbs/m}^3$) pounds of waste could include one standard lithium cell. Given that five pounds of solid waste are produced for disposal daily for each person, an equivalent of 238 person's waste would be needed daily for disposal with each lithium cell.

$$\frac{1190 \text{ lbs (necessary solid waste per cell)}}{5 \text{ lbs/person (solid waste per day)}} = 238 \text{ people}$$

While analysis indicates that maximum cyanide formation occurs when cells are discharged to a negative voltage, information supplied by ECOM and confirmed by laboratory test results (Figure 4) reveal that 1.70 volts is the point at which the voltage decreases rapidly in a standard cell, and is no longer functional. Thus, the 1.70 volt level would, in the majority of cases, be the point at which most cells were disposed of. The average soluble cyanide potentially available for release to the environment at this level was 22.0 mg per cell (based on laboratory test results). Applying the disposal density model at this concentration reveals that 2.6 m^3 of solid waste must be included with one standard lithium cell to insure an average leachate of less than or equal to 0.2 mg/l of cyanide. This represents daily disposal of one cell with the solid waste generated by 52 persons during that day.

Laboratory testing of modified lithium cells revealed an average maximum concentration of only 0.16 mg per cell (See Table 2). Applying the model at this concentration indicates that 0.019 m³ of solid waste must be included with each modified cell, or 2.6 cells disposed of daily with each person's solid waste (0.38 persons/cell/day).

Examination of these results indicates that municipal landfill disposal of standard lithium cells is probably not a workable disposal alternative under most field operation conditions. Most discharged cells would have to be transported back to a large military installation and periodically included with solid waste disposed of at that facility if sanitary landfills are to be utilized. The estimates of disposal density calculated using this model should also be considered with reservations. The model attempts to predict only the average concentration of cyanide in the leachate. Additional data on the diffusion rate of the cell components and the porosity and weathering of the soils where anion exchange sites develop, would be needed to calculate maximum leachate concentrations. By assuming equal distribution of the cyanide within a layer of the landfill it allowed us to arrive at some disposal density value which might assist ECOM officials in their evaluations of disposal alternatives. This calculation, however, when applied to actual laboratory leachate testing data for sandy loam soil, estimated that the leachate would contain 4.13 mg/l cyanide assuming the standard cell contained the 40.59 mg per cell collected in the leachate. Results of leachate testing revealed that the maximum concentration of the leachate was 19.5 mg/l of cyanide per cell. From these data it can be seen that the model does not correctly estimate the maximum leachate concentration. In evaluating these disposal density calculations, laboratory data may serve as a better indicator of actual leachate concentrations than those estimates produced from the model.

III. RECOMMENDATIONS FOR DISPOSAL

A. Summary of Conclusions

Standard lithium-organic electrolyte/SO₂ cells can release high levels of cyanide, when the components of the cell are exposed to the environment. Laboratory results show that an average discharged cell releases approximately 22 mg of cyanide and an undischarged cell 1.6 mg of cyanide. The average fatal dose for humans is between 50 and 60 mg.¹⁶ The cyanide apparently results from a chemical reaction between lithium and acetonitrile in the discharged cell in the absence of SO₂. In addition to cyanide, which is the most toxic of the disposed standard cell constituents, sulfur dioxide and lithium exert less toxic effects on plants and animals.

The lithium cell also has some potentially hazardous properties, such as a tendency to flame when exposed to moisture and the fact that the cell is pressurized. These factors need to be carefully considered when decisions regarding disposal are involved, but these factors were not considered within the scope of this program.

Based upon environmental considerations of disposal in landfills, there undoubtedly exists some volume of solid waste which could contain either a discharged or charged standard lithium cell and insure that the leachate from the cell would meet environmental standards. However, attempts to calculate a cell/solid waste disposal ratio have been extremely difficult to accomplish. The disposal density calculations presented in this report were based upon a very simple model of landfill leachate and are only capable of estimating the average concentration of a cell constituent in the leachate.

The development of the simple landfill disposal density model was accomplished to provide ECOM with some rough guidelines of how many cells can be disposed when mixed with solid waste. However, it should be emphasized that experience in dealing with federal and state regulatory agencies has shown that consideration of disposal density factors or dilution factors for contaminants will not stand alone as a rationale for disposal methods. Additional data must be collected at the actual disposal sites. This requires monitoring of groundwater quality in the immediate vicinity, preferably from monitoring wells located within or adjacent to the landfill.

B. Disposal Recommendations

Versar's recommendations for the disposal of the standard lithium-organic electrolyte/SO₂ cell (discharged and charged) are the following:

- The most environmentally safe disposal alternative for the cells is to place them in secured landfills or disposal ponds with provisions for leachate control and monitoring, documentation and runoff control.
- Sanitary landfills or special landfills can be used where the cells are dispersed in large quantities of solid waste in a carefully controlled manner to produce a leachate containing less than 0.2 mg/l concentration of cyanide. However, this disposal practice should be used only with landfills where leachate monitoring is practiced on a routine basis.

Versar's recommendation for the disposal of the modified lithium organic electrolyte/SO₂ cell is that the cell can be disposed of with the normally collected solid waste in a sanitary landfill. The potential environmental effects posed by disposal of the modified cell are considered to be minimal.

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APPENDIX A
ANALYTICAL PROCEDURES

Laboratory analyses of lithium cell components present in distilled water solutions and column leachates were conducted using approved test procedures.¹ Specific parameters tested included lithium, acetonitrile, sulfite, cyanide, pH and conductivity. A description of the methods used during laboratory testing and the references from which they were selected are summarized in Table A-1.

TABLE A-1. Analytical Laboratory Procedures

<u>Parameter and Units</u>	<u>Method of Analysis</u>	<u>Reference</u>
Lithium (mg/l)	Flame emission	SM ² , 312A
Sulfite (mg/l-SO ₃)	Titrimetric, iodine-iodate	EPA ³ , p 285
Acetonitrile (mg/l)	Flame ionization, G-LC	ASTM ⁴ , D3371-74T
Cyanide (mg/l)	Manual Colorimetric, pyridine-barbituric acid	EPA, p 40
	Automated Colorimetric, pyridine-barbituric acid	Tech ⁵ , 315-74W
pH	Electrometric	EPA, p 239
Conductivity (µmhos/cm)	Wheatstone Bridge Conductimetry	EPA, p 275

Detailed procedures for analysis of cyanide and pH have been included in this appendix section.

A. Comparison of Cyanide Analysis Methods

Analysis of distilled water samples and column leachates containing soluble cyanide were performed using a Technicon Auto Analyzer II and a modification of their Industrial Method No. 315-74.⁵ This procedure is simply an automated version of the standard approved method in which cyanides are converted to cyanogen chloride by reaction with chloramine-T. This compound subsequently reacts with pyridine and barbituric acid to give a red color complex. In the standard Technicon cyanide procedure, the sample is passed through a UV source in the digestion phase of the analysis to break down cyanide which exists in metallic complexes, such as ferricyanide, cupricyanide, etc. This UV digestion is not included in the EPA approved manual procedures, so the Technicon method was modified to duplicate the manual analysis procedure.

The automated system provided greater precision and accuracy than the manual method and was far more sensitive to low concentrations of cyanide.

Published detection limits for the manual procedure are 0.10 mg/l. With the anticipated low concentration of cyanide in live standard lithium cells and modified cells it was felt that this exceeded the level of detection required for characterization of these cells. Thus, the automated procedure with its greater sensitivity (a detection limit of 0.005 mg/l) was selected for use in this program. To confirm the comparability of the two procedures, test samples were analyzed by both methods. These samples include live and discharged cell solution and various standards. Results of these analyses are summarized in Table A-2.

TABLE A-2. Comparison of Cyanide Methods

<u>Sample Type</u>	Automated Procedure <u>mg/l cyanide</u>	Manual Procedure <u>mg/l cyanide</u>
Live Cell I - 24 hours	0.094	<0.10
Live Cell I - 72 hours	0.094	<0.10
Live Cell I - 144 hours	0.088	<0.10
Live Cell II - 4 hours	0.087	<0.10
Live Cell II - 24 hours	0.064	<0.10
Live Cell II - 72 hours	0.146	<0.10
Live Cell II - 144 hours	0.128	<0.10
Discharged Cell I - 24 hours	43	41
Discharged Cell I - 72 hours	39	39
Discharged Cell I - 144 hours	28	26
Discharged Cell II - 4 hours	32	31
Discharged Cell II - 24 hours	33	32
Discharged Cell II - 72 hours	29	31
Discharged Cell II - 144 hours	25	23
0.05 mg/l Standard	0.048	<0.10
0.10 mg/l Standard	0.103	<0.10
1.00 mg/l Standard	0.99	0.97
10.0 mg/l Standard	10.0	10.2
50 mg/l Standard	50	50

B. Evaluation of Cyanide Analysis Method Using Cell Leachate Materials

To evaluate the accuracy and reliability of the cyanide analysis performed on samples of cell leachate and soluble cell constituents, it was important to determine if acetonitrile present in the samples was being broken down during the actual cyanide analysis and thus incorrectly being considered as soluble cyanide produced in the lithium cell. There were also some indications that certain constituents of the cell may have acted as interferences to the

cyanide analysis. Researchers indicate that sulfur and in particular sulfide may adversely affect the analysis. The following section describes the laboratory analysis performed to verify the cyanide values presented in this report.

1. Breakdown of Acetonitrile

To assure that cyanide results were reflective of actual cyanide and not due to dissociation caused by the method of analysis, an acetonitrile control was analyzed for cyanide. Analysis of a 787 mg/l acetonitrile standard revealed that only 8 mg/l of cyanide were present (a one percent dissociation of acetonitrile). In addition, previously analyzed lithium cell solutions were spiked with 10 mg/l known additions of acetonitrile and re-analyzed. Results presented in Table A-3 indicate no significant breakdown of acetonitrile during subsequent analysis.

TABLE A-3. Analysis of Lithium Cell Solutions Spiked with 10 mg/l Acetonitrile

<u>Cyanide Concentration of Samples Prior to Acetonitrile Addition</u>	<u>Cyanide Concentration of Samples Following Acetonitrile Addition</u>
0.92	0.90
2.3	2.1
8.0	8.0
4.0	4.1
10.2	10.4
14.8	15.0
25.2	25.0

Another indication that cyanide concentrations were a result of cell component alteration was that the two live cells showed cyanide levels greatly below that of discharged cells. This would not be the case had the actual analysis procedure led to acetonitrile dissociation. Based on these two facts we concluded that cyanide results reflect actual cyanide levels due to acetonitrile dissociation in discharged cells.

2. Effects of Interference

Research indicates that when sulfite is present in a highly basic solution (such as that recorded in the lithium cell solutions), it will be reduced to sulfide and/or free sulfur. Sulfide, if present in the sample, can convert

cyanide (CN^-) to thiocyanate (SCN^-), especially at high pH.

To determine if sulfide was interfering with cyanide analysis of lithium cell solutions, samples were analyzed both with and without the sulfide removed. Before stabilizing the sample by raising the pH for the preservation of cyanide content, half of the sample was treated with excess powdered lead carbonate. The sample was stirred, allowed to stand and precipitate filtered out with a 0.45 micron glass fiber filter. Results of this comparative testing are summarized in Table A-4.

TABLE A-4. Analysis of Lithium Cell Solutions With and Without Sulfide Removal

<u>Cyanide Concentration of Samples Without Sulfide Removed</u>	<u>Cyanide Concentration of Samples With Sulfide Removed</u>
4.0	4.1
8.8	8.8
6.8	6.6
10.2	10.3
14.8	15.0
25.2	25.0

These data indicate that sulfide had no effect on cyanide analysis performed during this study. It should, however, be noted that these samples required dilution prior to analysis because of the high cyanide levels present. Problems were encountered when live standard cells and modified cells which contained trace quantities of cyanide were analyzed. These samples required no dilution prior to analysis. During testing a white precipitate was produced which made further cyanide analysis impossible. The remaining portions of these samples were then split. Sulfur was removed from one of these aliquots and the other simply diluted. Both portions were then re-analyzed. Results revealed that by diluting the samples to remove the interference, we had reduced the cyanide concentration to below the 0.005 mg/l detection limit. No difficulties with interferences were observed in the subsequent analysis of the treated aliquots. It appears that because of the dilutions required to most samples prior to analysis, sulfide did not interfere with cyanide results of the lithium cell solutions or leachates.

References

1. U.S. EPA. 1976. Guidelines Establishing Test Procedures for Analysis an Pollutants. *Federal Register*, Washington, D.C. Vol. 41 (232): 52781-52784.
2. American Public Health Association, American Water Works Association and Water Pollution Control Federation. 1976. *Standard Methods for the Examination of Water and Wastewater*. 14th ed., American Public Health Association, Inc. pp. 219-221.
3. U.S. EPA. 1974. *Methods for Chemical Analysis of Water and Wastes*, EPA-625/6-74-003. Cincinnati, Chio. pp. 40-48, 239-40.
4. ASTM. 1977. *Annual Book of ASTM Standards. Water Analysis*. Philadelphia, Pennsylvania, pp. 606-608.
5. Technicon Instruments Corporation. 1974. *Operation Manual for Technicon Autoanalyzer II System*. Technical Publication 315-74W. Technicon Instruments Corporation, Tarrytown, New York.

Technicon AutoAnalyzer™ III

INDUSTRIAL METHOD No. 315-74W

DATE RELEASED: AUGUST 1974

CYANIDE IN WATER AND WASTEWATER (RANGE: 0-500 $\mu\text{g/l}$) (UV DIGESTION + DISTILLATION)

GENERAL DESCRIPTION

Cyanides are converted to cyanogen chloride by reaction with chloramine-T which subsequently reacts with pyridine and barbituric acid to give a red-colored complex. Cyanide often exists in metallic complexes, such as ferricyanide, zincocyanide, cupricyanide, etc. Therefore, a digestion distillation stage has been incorporated into this cyanide system. This stage converts the metallo-cyanides into simple cyanides which, upon acidification, form hydrogen cyanide.^{1,2,3}

PERFORMANCE AT 30 SAMPLES PER HOUR

USING AQUEOUS STANDARDS

Sensitivity at 500 $\mu\text{g/l}$ 0.70 absorbance units

Coefficient of Variation at 300 $\mu\text{g/l}$ 0.27%

Detection Limit 5 $\mu\text{g/l}$

REAGENTS

DISTILLATION REAGENT

(Technicon No. T01-5017)

Phosphoric Acid, 85% (H_3PO_4)	250	ml
Hypophosphorus Acid	50	ml
Distilled Water, q.s.	1000	ml

Preparation:

Carefully add 250 ml of 85% phosphoric acid and 50 ml of hypophosphorus acid to 700 ml of distilled water and dilute to one liter with distilled water.

PHOSPHATE BUFFER, pH 5.2

Potassium Dihydrogen Phosphate (KH_2PO_4) 13.6 g

¹ Goulden, P.D., Afghan, B.K. and Brooksbank, P., *Anal. Chem.* 44 (1972).

² ASTM. *Standard Methods of Test for Cyanides in Water*, p. 553-561 (1972).

³ *Standard Methods for the Examination of Water and Wastewater*, 13th Edition, 1971, p. 404-406.

Disodium Hydrogen Phosphate

(Na_2HPO_4)	0.28	g
Distilled Water, q.s.	1000	ml
Brij-35* (Technicon No. T21-0110)	0.5	ml

Preparation:

Dissolve 13.6 g of potassium dihydrogen phosphate and 0.28 g of disodium phosphate in 900 ml of distilled water and dilute to one liter. Add 0.5 ml of Brij-35 and mix.

CHLORAMINE-T

Chloramine-T**	2.0	g
($\text{C}_7\text{H}_7\text{ClNO}_2\text{SNa} \cdot 3\text{H}_2\text{O}$)	500	ml
Distilled Water		

Preparation:

Dissolve 2.0 g of chloramine-T in 500 ml of distilled water.

PYRIDINE BARBITURIC ACID REAGENT

Barbituric Acid ($\text{C}_4\text{H}_4\text{N}_2\text{O}_3$)	15	g
Pyridine ($\text{C}_5\text{H}_5\text{N}$)	75	ml
Hydrochloric Acid, conc. (HCl)	15	ml
Distilled Water, q.s.	1000	ml

Preparation:

Place 15 g of barbituric acid in a one liter beaker and add enough water (about 100 ml) to wash the sides of the beaker and wet the barbituric acid. Add 75 ml of pyridine and mix. Add 15 ml of HCl (sp. gr. 1.19) and mix. Dilute to about 900 ml with distilled water and mix until all the barbituric acid has dissolved. Transfer the solution to a one liter flask and dilute to volume with distilled water.

STANDARDS

STOCK STANDARD A, 100 mg/l

Potassium Cyanide (KCN)	0.250	g
Sodium Hydroxide, 0.1 N (NaOH), q.s.	1000	ml

* Trademark of Atlas Chemical Industries, Inc.

** Available from Eastman Kodak #1022.



TECHNICON INDUSTRIAL SYSTEMS / TARRYTOWN, N.Y. 10591
A DIVISION OF TECHNICON INSTRUMENTS CORPORATION

Preparation:

Dissolve 0.250 g of potassium cyanide in 800 ml of 0.1 N sodium hydroxide and dilute to one liter with 0.1 N of sodium hydroxide.

WARNING: AVOID SKIN CONTACT WITH POTASSIUM CYANIDE.

STOCK STANDARD B, 10 mg/l

Dilute to 100 ml of stock A to one liter with 0.1 N sodium hydroxide.

WORKING STANDARDS

<u>ml Stock B</u>	<u>µg/l</u>
1	100
2	200
3	300
4	400
5	500

Preparation:

Pipette stock B into a 100 ml volumetric flask and dilute to volume with 0.01 N sodium hydroxide.

OPERATING NOTES

1. This system should be operated in a hood or a well-ventilated area.
2. Set temperature of the heating bath at 150 °C.
3. Flow rate of cooling water through the distillation apparatus should be approximately 750 ml per

minute at about 14 °C. See Instruction Manual TA1-0213-00 for operation of the distillation head.

4. The chemistry is linear up to 300 µg/l. A Linearizer is required to obtain a linear response over the whole range.
5. Before running the method, position the controls of the Modular Printer as follows:

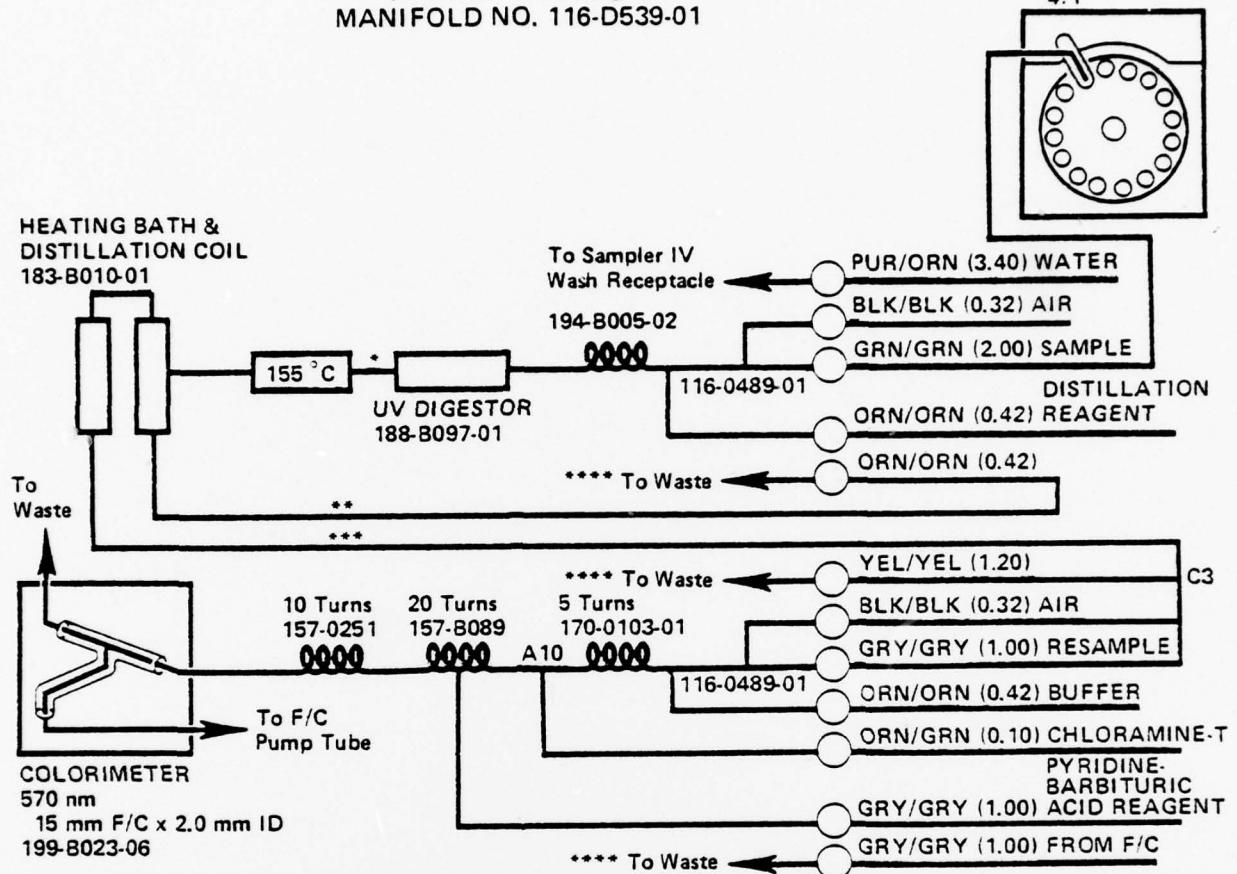
<u>CONTROL</u>	<u>POSITION</u>
MODE Switch	Normal
SAMPLING RATE Switch	30
RANGE Switch	500
DECIMAL Switch	000.

Details of Modular Printer Operation are provided in Technical Publication No. TA1-0278-10.

6. Do not use the Modular Printer without a Linearizer.
7. Alternate ranges may be obtained by utilization of the Std Cal control on the Colorimeter.
8. Since HCN is extremely toxic, enough sodium hydroxide to keep the solution basic should be added to the waste containers.
9. When installing replacement light source in UV Digestor (188-B097-01), allow burn-in of 12 to 24 hours to permit new UV lamp to equilibrate. (New lamps may generate undesirable levels of ozone, which may reduce yield.)

CYANIDE IN WATER & WASTEWATER (UV DIGESTION + DISTILLATION)
 (RANGE: 0-500 $\mu\text{g/l}$)
 MANIFOLD NO. 116-D539-01

SAMPLER IV
 30/Hr
 4:1



- * 0.050 KEL-F[†] (562-3014-01)
- ** 0.100 ACIDFLEX (116-0538-17)
- *** 0.034 POLYETHYLENE (562-2004-01)
- **** SEE OPERATING NOTE 8.

[†] TRADEMARK OF 3-M COMPANY.

CYANIDE, Total

STORET NO. 00720

1. Scope and Application

- 1.1 This method is applicable to the determination of cyanide in drinking, surface, and saline waters, domestic and industrial wastes.
- 1.2 The titration procedure using silver nitrate with p-dimethylamino-benzalrhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/l (0.2 mg/200 ml of absorbing liquid).
- 1.3 The colorimetric procedure is used for concentrations below 1 mg/l of cyanide and is sensitive to about 0.02 mg/l.

2. Summary of Method

- 2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.
- 2.2 In the colorimetric measurement the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone or 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.
- 2.3 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3. Definitions

- 3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of cuprous ion.

4. Sample Handling and Preservation

- 4.1 The sample should be collected in plastic bottles of 1 liter or larger size. All bottles must be thoroughly cleansed and thoroughly rinsed to remove soluble material from containers.
- 4.2 Samples must be preserved with 2 ml of 10 N sodium hydroxide per liter of sample ($\text{pH} \geq 12$) at the time of collection.

- 4.3 Samples should be analyzed as rapidly as possible after collection. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain temperature at 4°C.
- 4.4 Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.

5. Interferences

- 5.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure (8.1 through 8.5).
- 5.2 Sulfides adversely affect the colorimetric and titration procedures. If a drop of the sample on lead acetate test paper indicates the presence of sulfides, treat 25 ml more of the stabilized sample ($\text{pH} \geq 12$) than that required for the cyanide determination with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure the sample to be used for analysis. Avoid a large excess of cadmium and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material.
- 5.3 Fatty acids will distill and form soaps under the alkaline titration conditions, making the end point almost impossible to detect.
 - 5.3.1 Acidify the sample with acetic acid (1+9) to pH 6.0 to 7.0.

Caution: This operation must be performed in the hood and the sample left there until it can be made alkaline again after the extraction has been performed.
 - 5.3.2 Extract with iso-octane, hexane, or chloroform (preference in order named) with a solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the fatty acids below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is completed, immediately raise the pH of the sample to above 12 with NaOH solution.

6. Apparatus

- 6.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling

flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

6.2 Microburet, 5.0 ml (for titration).

6.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger.

7. Reagents

7.1 Sodium hydroxide solution: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.

7.2 Cadmium carbonate: powdered.

7.3 Ascorbic acid: crystals.

7.4 Cuprous Chloride Reagent: Weigh 20 g of finely powdered Cu_2Cl_2 into an 800 ml beaker. Wash twice, by decantation, with 250 ml portions of dilute sulfuric acid (H_2SO_4 , 1 + 49) and then twice with water. Add about 250 ml of water and then hydrochloric acid (HCl, sp gr 1.19) in 1/2 ml portions until the salt dissolves (See Note 1). Dilute to 1 liter with distilled water and store in a tightly stoppered bottle containing a few lengths of pure copper wire or rod extending from the bottom to the mouth of the bottle (See Note 2).

Note 1: The reagent should be clear; dark discoloration indicates the presence of cupric salts.

Note 2: If it is desired to use a reagent bottle of smaller volume, it should be kept completely filled and tightly stoppered. Refill it from the stock solution after each use.

7.5 Sulfuric acid: concentrated.

7.6 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in 1 liter of distilled water. Refrigerate this solution.

7.7 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 1 liter of distilled water. Standardize with 0.0192 N AgNO_3 . Dilute to appropriate concentration so that 1 ml = 1 mg CN.

7.8 Standard cyanide solution, intermediate: Dilute 10.0 ml of stock (1 ml = 1 mg CN) to 1000 ml with distilled water (1 ml = 10 μg).

7.9 Standard cyanide solution: Prepare fresh daily by diluting 100.0 ml of intermediate cyanide solution to 1000 ml with distilled water and store in a glass stoppered bottle. 1 ml = 1.0 μg CN (1.0 mg/1).

7.10 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g AgNO_3 crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried AgNO_3 , dissolve in distilled water, and dilute to 1000 ml (1 ml = mg CN).

7.11 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-amino-benzalrhodanine in 100 ml of acetone.

7.12 Chloramine T solution: Dissolve 1.0 g of white, water soluble Chloramine T in 100 ml of distilled water and refrigerate until ready to use. Prepare fresh weekly.

7.13 Color Reagent - One of the following may be used:

7.13.1 Pyridine-Barbituric Acid Reagent: Place 15 g of barbituric acid in a 250 ml volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 ml of pyridine and mix. Add 15 ml of HCl (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 ml with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

7.13.2 Pyridine-pyrazolone solution:

7.13.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution. Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 ml of distilled water, heat to 60°C with stirring. Cool to room temperature.

7.13.2.2 3,3'Dimethyl-1,1'-diphenyl-[4,4'-bi-2 pyrazoline]-5,5'dione (bispyrazolone). Dissolve 0.01 g of bispyrazolone in 10 ml of pyridine.

7.13.2.3 Pour solution (7.13.2.1) through nonacid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.13.2.2) collecting the filtrate in the same container as filtrate from (7.13.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

8. Procedure

- 8.1 Place 500 ml of sample, or an aliquot diluted to 500 ml in the 1 liter boiling flask. Add 50 ml of sodium hydroxide (7.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber and trap in the train.
- 8.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

Caution: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

- 8.3 Slowly add 25 ml conc. sulfuric acid (7.5) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 min. Pour 10 ml of Cu_2Cl_2 reagent (7.4) into the air inlet and wash down with a stream of water.
- 8.4 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.
- 8.5 Drain the solution from the absorber into a volumetric flask and bring up to volume with distilled water washings from the absorber tube.
- 8.6 Withdraw 50 ml of the solution from the volumetric flask and transfer to a 100 ml volumetric flask. Add 15 ml of sodium phosphate solution (7.6) and 2.0 ml of Chloramine T solution (7.12) and mix. Immediately add 5.0 ml pyridine-barbituric acid solution (7.13.1), or pyridine-pyrazolone solution (7.13.2.3), mix and bring to mark with distilled water and mix again.
- 8.7 For pyridine-pyrazolone solution allow 40 minutes for color development then read absorbance at 620 nm in a 1 cm cell. When using pyridine-barbituric acid, allow 8 minutes for color development then read absorbance at 578 nm in a 1.0 cm cell within 15 minutes.
- 8.8 Prepare a series of standards by diluting suitable volumes of standard solution to 500.0 ml with distilled water as follows:

ml of Standard Solution (1.0 = 1 μg CN)	Conc., When Diluted to 500 ml, mg/1 CN
0 (Blank)	0
5.0	0.01
10.0	0.02
20.0	0.04
50.0	0.10
100.0	0.20
150.0	0.30
200.0	0.40

- 8.8.1 Standards must be treated in the same manner as the samples, as outlined in (8.1) through (8.7) above.
 - 8.8.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations.
 - 8.8.3 Subsequently, at least two standards (a high and a low) should be treated as in (8.8.1) to verify standard curve. If results are not comparable ($\pm 20\%$), a complete new standard curve must be prepared.
 - 8.8.4 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.8) or the working standard (7.9) to insure a level of $20\mu\text{g}/\text{l}$ or a significant increase in absorbance value. Proceed with the analysis as in Procedure (8.8.1) using the same flask and system from which the previous sample was just distilled.
 - 8.9 Alternatively, if the sample contains more than 1 mg of CN transfer the distillate, or a suitable aliquot diluted to 250 ml, to a 500 ml Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator.
 - 8.10 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.
 - 8.11 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5 or 10 ml microburet may be conveniently used to obtain a more precise titration.
9. Calculation
- 9.1 Using the colorimetric procedure, calculate concentration of CN, mg/l, directly from prepared standard curve compensating for sample dilution if less than 500 ml was used for distillation.
 - 9.2 Using the titrimetric procedure, calculate concentration of CN as follows:

$$\text{CN, mg/l} = \frac{(\text{A}-\text{B}) 1000}{\text{ml original sample}} \times \frac{250}{\text{ml of aliquot titrated}}$$

where:

A = volume of AgNO_3 for titration of sample.

B = volume of AgNO_3 for titration of blank.

10. Precision and Accuracy

- 10.1 In a single laboratory (MDQARL), using mixed industrial and domestic waste samples at concentrations of 0.06, 0.13, 0.28 and 0.62 mg/l CN, the standard deviations were ± 0.005 , ± 0.007 , ± 0.031 , and ± 0.094 , respectively.

10.2 In a single laboratory (MDQARL), using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/l CN, recoveries were 85% and 102%, respectively.

Bibliography

1. Bark, L. S., and Higson, H. G. "Investigation of Reagents for the Colorimetric Determination of Small Amounts of Cyanide". *Talanta*, 2:471-479 (1964).
2. Elly, C. T. "Recovery of Cyanides by Modified Serfass Distillation". *Journal Water Pollution Control Federation*, 40:848-856 (1968).
3. ASTM Standards, Part 23, Water: Atmospheric Analysis, p 498, Method D2036-72 Referee Method A (1973).

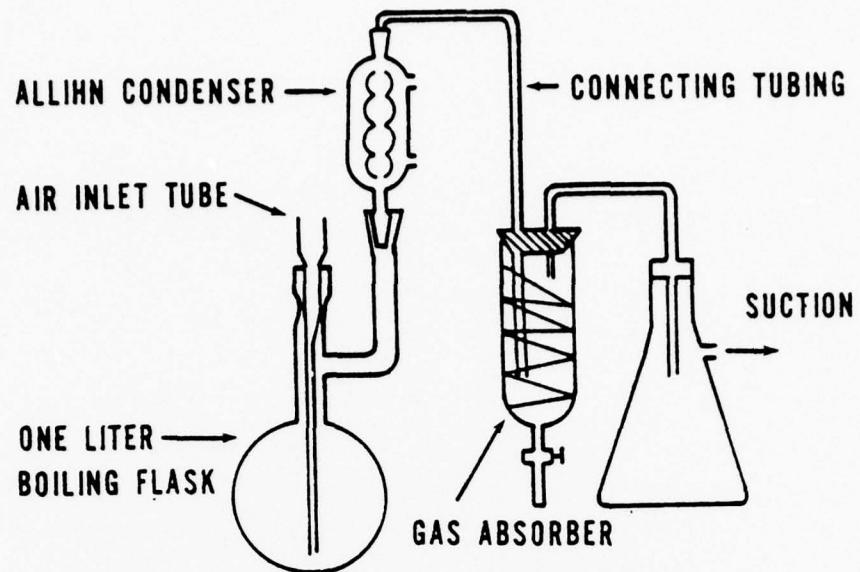


FIGURE 1
CYANIDE DISTILLATION APPARATUS

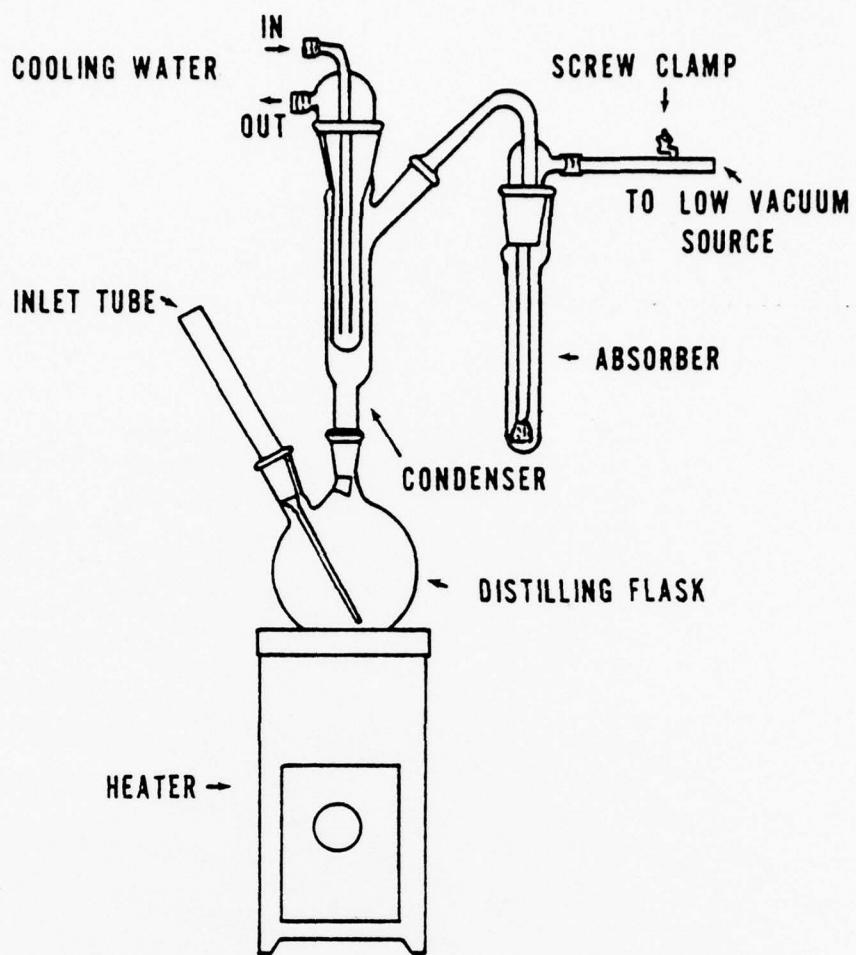


FIGURE 2
CYANIDE DISTILLATION APPARATUS

pH

STORET NO. 00400

1. Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

2. Summary of Method

2.1 The pH of a sample is an electrometric measurement, using either a glass electrode in combination with a reference potential (saturated calomel electrode) or a combination electrode (glass and reference).

3. Comments

3.1 The sample must be analyzed as soon as practical; preferably within a few hours. Do not open sample bottle before analyses.

3.2 Oil and greases, by coating the pH electrode, may interfere by causing sluggish response.

3.3 At least three buffer solutions must be used to initially standardize the instrument. They should cover the pH range of the samples to be measured.

3.4 Field pH measurements using comparable instruments are reliable.

4. Precision and Accuracy

4.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

Increment as pH Units	Precision as Standard Deviation pH Units	Accuracy as	
		Bias, %	Bias, pH Units
3.5	0.10	-0.29	-0.01
3.5	0.11	-0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	-0.03	-0.002
8.0	0.13	-0.12	-0.01
8.0	0.12	+0.16	+0.01

(FWPCA Method Study 1, Mineral and Physical Analyses)

4.2 In a single laboratory (MDQARL), using surface water samples at an average pH of 7.7, the standard deviation was ± 0.1 .

5. Reference

5.1 The procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, p 276, Method 144 A (1971).

ASTM Standards, Part 23, Water: Atmospheric Analysis, p 186, Method D1293-65 (1973).

APPENDIX B
LABORATORY RESULTS

AD-A059 512

VERSAR INC SPRINGFIELD VA
INVESTIGATION OF THE ENVIRONMENTAL CONSEQUENCES OF DISPOSAL OF --ETC(U).
MAR 78 K CRUMRINE, E JUERGENS, C COLBURN DAAB07-76-C-1752

UNCLASSIFIED

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DDC

TABLE B-1 CYANIDE CONCENTRATIONS IN LIVE STANDARD LITHIUM CELLS
(No Discharge)

<u>Cyanide Concentration (mg/l)</u>	<u>Deviations</u>	<u>Sums of Squares</u>
$x_{2.8,24}$	$ x_{2.8,24} - \bar{x}_{2.8,24} $	$(x_{2.8,24} - \bar{x}_{2.8,24})^2$
0.30	0.015	0.000225
0.36	0.045	0.002025
0.25	0.065	0.004225
0.63	0.315	0.099225
0.28	0.035	0.001225
0.25	0.065	0.004225
0.20	0.115	0.013225
0.23	0.085	0.007225
0.41	0.095	0.009025
0.24	0.075	0.005625
$\Sigma = 3.15$		$\Sigma = .146250$
$\bar{x}_{2.8,24} = 0.32$		$s^2 = 0.016$
		$\sigma = 0.13$
 $x_{2.8,48}$	 $ x - \bar{x} $	 $(x - \bar{x})^2$
0.77	0.468	0.219024
0.14	0.162	0.026244
0.18	0.122	0.014884
0.23	0.072	0.005184
0.20	0.102	0.010404
0.28	0.022	0.000484
0.22	0.082	0.006724
0.31	0.008	0.000064
0.43	0.128	0.016384
0.26	0.042	0.001764
$\Sigma = 3.02$		$\Sigma = .301160$
$\bar{x}_{2.8,48} = 0.30$		$s^2 = 0.033$
		$\sigma = 0.18$

TABLE B-2 CYANIDE CONCENTRATIONS IN STANDARD LITHIUM CELLS
DISCHARGED TO THE 2.40 VOLT LEVEL

<u>Cyanide Concentration (mg/l)</u>	<u>Deviations</u>	<u>Sums of Squares</u>
$X_{2.4,24}$	$ X - \bar{X} $	$(X - \bar{X})^2$
0.30	0.624	0.3894
0.52	0.404	0.1632
1.06	0.136	0.0185
1.80	0.876	0.7674
2.60	1.676	2.8090
0.14	0.784	0.6146
0.56	0.364	0.1325
0.70	0.224	0.0502
0.64	0.284	0.0806
$\Sigma = 8.32$		$\Sigma = 5.0254$
$\bar{X}_{2.4,24} = 0.92$		$s^2 = 0.628$
		$\sigma = 0.79$
 $X_{2.4,48}$	 $ X - \bar{X} $	 $(X - \bar{X})^2$
0.34	0.86	0.7396
0.58	0.62	0.3844
0.92	0.28	0.0784
2.3	1.10	1.21
4.0	2.80	7.84
0.21	0.99	0.9801
0.66	0.54	0.2916
0.77	0.43	0.1849
1.00	0.20	0.0400
$\Sigma = 10.78$		$\Sigma = 11.749$
$\bar{X}_{2.4,48} = 1.20$		$s^2 = 1.468$
		$\sigma = 1.21$

TABLE B-3 CYANIDE CONCENTRATIONS IN STANDARD LITHIUM CELLS
DISCHARGED TO 2.00 VOLT LEVEL

<u>Cyanide Concentration (mg/l)</u>	<u>Deviations</u>	<u>Sum of Squares</u>
$x_{2.0,24}$	$ x - \bar{x} $	$\sum (x - \bar{x})^2$
4.0	1.6	2.56
8.8	3.2	10.24
4.4	1.2	1.44
4.0	1.6	2.56
6.8	1.2	1.44
8.8	3.2	10.24
4.0	1.6	2.56
6.4	0.8	0.64
3.2	2.4	5.76
$\Sigma = 50.4$		$\Sigma = 37.44$
$\bar{x} = 5.6$		$s^2 = 4.68$
		$\sigma = 2.16$
 $x_{2.0,48}$	 $ x - \bar{x} $	 $\sum (x - \bar{x})^2$
4.0	1.3	1.69
8.0	2.7	7.29
3.2	2.1	4.41
3.8	1.5	2.25
6.4	1.1	1.21
8.4	3.1	9.61
4.0	1.3	1.69
6.8	1.5	2.25
3.2	2.1	4.41
$\Sigma = 47.8$		$\Sigma = 34.81$
$\bar{x} = 5.3$		$s^2 = 4.35$
		$\sigma = 2.08$

TABLE B-4 CYANIDE CONCENTRATIONS IN STANDARD LITHIUM CELLS
DISCHARGED TO THE 1.70 VOLT LEVEL

<u>Cyanide Concentration (mg/l)</u>	<u>Deviations</u>	<u>Sums of Squares</u>
$x_{1.7,24}$	$ x - \bar{x} $	$\sum (x - \bar{x})^2$
1.6	2.8	7.84
3.75	0.65	0.4225
6.4	2.0	4.00
10.2	5.8	33.64
2.65	1.75	3.0625
4.0	0.40	0.16
4.25	0.15	0.0225
5.2	0.8	0.64
1.6	2.8	7.84
$\Sigma = 39.35$		$\Sigma = 57.6275$
$\bar{x}_{1.7,24} = 4.4$		$s^2 = 7.203$
		$\sigma = 2.684$
 $x_{1.7,48}$	 $ x - \bar{x} $	 $\sum (x - \bar{x})^2$
1.6	2.69	7.2361
3.69	0.60	0.36
6.4	2.11	4.4521
10.0	5.71	32.6041
2.4	1.89	3.5721
3.7	0.59	0.3481
4.05	0.24	0.0576
5.2	0.91	0.8281
1.55	2.74	7.5076
$\Sigma = 38.59$		$\Sigma = 56.9658$
$\bar{x}_{1.7,48} = 4.29$		$s^2 = 7.121$
		$\sigma = 2.67$

TABLE B-5

CYANIDE CONCENTRATIONS IN STANDARD LITHIUM CELLS
DISCHARGED TO THE 1.70 VOLT LEVEL AND PLACED IN
BUFFERED SOLUTION

Cyanide Concentration (mg/l)	Deviations	Sums of Squares
$\bar{X}_{1.7,24}$	$ X - \bar{X} $	$\Sigma (X - \bar{X})^2$
14.8	5.28	27.87
8.0	1.52	2.31
10.4	0.88	0.77
4.0	5.52	30.47
7.6	1.92	3.69
7.6	1.92	3.69
6.0	3.52	12.39
11.2	1.68	2.82
14.4	4.88	23.81
<u>11.2</u>	<u>1.68</u>	<u>2.82</u>
$\Sigma = 95.2$		$\Sigma = 110.64$
$\bar{X}_{1.7,24} = 9.52$		$S^2 = 12.29$
		$\sigma = 3.51$
 $X_{1.7,48}$	 $ X - \bar{X} $	 $\Sigma (X - \bar{X})^2$
16.0	6.32	39.94
7.6	2.08	4.33
10.4	0.72	0.52
3.6	6.08	36.97
7.6	2.08	4.33
7.6	2.08	4.33
6.4	3.28	10.76
11.6	1.92	3.69
14.8	5.12	26.21
<u>11.2</u>	<u>1.52</u>	<u>2.31</u>
$\Sigma = 96.8$		$\Sigma = 124.15$
$X_{1.7,48} = 9.68$		$S^2 = 13.79$
		$\sigma = 3.71$

TABLE B-6 CYANIDE CONCENTRATION IN STANDARD LITHIUM CELLS DISCHARGED TO THE 0.10 VOLT LEVEL

<u>Cyanide Concentration (mg/l)</u>	<u>Deviations</u>	<u>Sums of Squares</u>
$x_{0.1,24}$		
6.6	10.33	106.7089
17.2	0.27	.0729
16.8	.13	.0169
11.0	5.93	35.1649
25.8	8.87	78.6769
25.2	8.27	68.3929
17.0	0.07	.0049
20.4	3.47	12.0409
12.4	4.53	20.5209
$\Sigma = 152.4$		$\Sigma = 321.6001$
$\bar{x}_{0.1,24} = 16.93$		$s^2 = 40.200$
		$\sigma = 6.34$
6.6	10.56	111.5136
17.4	0.24	.0576
16.0	1.16	1.3456
11.6	5.56	30.9136
25.2	8.04	64.6416
25.6	8.44	71.2336
18.8	1.64	2.6896
20.8	3.64	13.2496
12.4	4.76	22.6576
$\Sigma = 154.4$		$\Sigma = 318.3024$
$\bar{x}_{0.1,48} = 17.16$		$s^2 = 39.788$
		$\sigma = 6.31$

TABLE B-7 CYANIDE CONCENTRATIONS IN STANDARD LITHIUM CELLS
DISCHARGED TO THE 0.10 VOLT LEVEL AND PLACED IN
BUFFERED SOLUTION

Cyanide Concentration (mg/l)	Deviations	Sums of Squares
$\bar{x}_{0.1,24}$	$ x - \bar{x} $	$\sum (x - \bar{x})^2$
2.0	5.56	30.9136
14.0	6.44	41.4736
7.2	0.36	0.1296
5.6	1.96	3.8416
5.2	2.36	5.5696
6.0	1.56	2.4336
9.6	2.04	4.1616
13.2	5.64	31.8096
8.0	0.44	0.1936
4.8	2.76	7.6176
$\Sigma = 75.6$		$\Sigma = 128.1440$
$\bar{x}_{0.1,24} = 7.56$		$S^2 = 14.24$
		$\sigma = 3.77$

$\bar{x}_{0.1,48}$	$ x - \bar{x} $	$\sum (x - \bar{x})^2$
2.0	5.56	30.9136
14.8	7.24	52.4176
8.0	0.44	0.1936
5.6	1.96	3.8416
5.6	1.96	3.8416
5.2	2.36	5.5696
9.2	1.64	2.6896
13.2	5.64	31.8096
7.6	0.04	0.0016
4.4	3.16	9.9856
$\Sigma = 75.6$		$\Sigma = 141.2640$
$\bar{x}_{0.1,48} = 7.56$		$S^2 = 15.70$
		$\sigma = 3.96$

TABLE B-8

CYANIDE CONCENTRATIONS IN STANDARD LITHIUM CELLS
DISCHARGED TO NEGATIVE VOLTAGECyanide Concentration
(mg/l) $\bar{x}_{-3.9,24}$

18.8	0.76
12.8	6.76
28.0	8.44
22.8	3.24
18.8	0.76
19.2	0.36
12.8	6.76
25.6	6.04
19.2	0.36
<u>17.6</u>	<u>1.96</u>

 $\Sigma = 195.6$
 $\bar{x}_{-3.9,24} = 19.56$
Deviations
 $|X - \bar{X}|$

Sums of Squares

 $\Sigma (X - \bar{X})^2$

0.5776
45.6976
71.2336
10.4976
0.5776
0.1296
45.6976
36.4816
0.1296
<u>3.8416</u>

 $\Sigma = 214.8640$
 $S^2 = 23.87$
 $\sigma = 4.89$
 $\bar{x}_{-3.9,48}$ | $X - \bar{X}$ | $\Sigma (X - \bar{X})^2$

6.4	7.66
10.2	3.86
18.0	3.94
16.8	2.74
15.6	1.54
14.8	0.74
10.4	3.66
.. 17.6 ..	3.54
16.0	1.94
<u>14.8</u>	<u>0.74</u>

 $\Sigma = 140.6$
 $\bar{x}_{-3.9,48} = 14.06$

58.6756
14.8996
15.5236
7.5076
2.3716
0.5476
13.3956
12.5316
3.7636
<u>0.5476</u>

 $\Sigma = 129.7640$
 $S^2 = 14.42$
 $\sigma = 3.80$

TABLE B-9 CYANIDE CONCENTRATIONS IN MODIFIED LITHIUM CELLS
DISCHARGED TO THE 1.70 VOLT LEVEL

Cyanide Concentration (mg/1)	Deviations	Sums of Squares
	$ X - \bar{X} $	$\Sigma (X - \bar{X})^2$
$\bar{X}_{1.7,24}$		
0.024	0.008	0.000064
0.044	0.012	0.000144
0.038	0.006	0.000036
0.038	0.006	0.000036
0.030	0.002	0.000004
0.016	0.016	0.000256
0.036	0.004	0.000016
0.032	0	0
0.030	0.002	0.000004
0.028	0.004	0.000016
$\Sigma = 0.316$		$\Sigma = 0.000576$
$\bar{X}_{1.7,24} = 0.032$		$S^2 = 0.0001$
		$\sigma = 0.008$
$\bar{X}_{1.7,48}$		$\Sigma (X - \bar{X})^2$
0.034	0.003	0.000009
0.030	0.001	0.000001
0.022	0.009	0.000081
0.060	0.029	0.000841
0.026	0.005	0.000025
0.028	0.003	0.000009
0.018	0.013	0.000169
0.036	0.005	0.000025
0.024	0.007	0.000049
0.028	0.003	0.000009
$\Sigma = 0.306$		$\Sigma = 0.001218$
$\bar{X}_{1.7,48} = 0.031$		$S^2 = 0.0001$
		$\sigma = 0.012$

TABLE B-10

CYANIDE CONCENTRATIONS IN MODIFIED LITHIUM CELLS
DISCHARGED TO THE NEGATIVE VOLTAGECyanide Concentration
(mg/l) $x_{3.8,24}$ DeviationsSums of Squares

0.024	0.002	0.000004
0.024	0.002	0.000004
0.020	0.006	0.000036
0.024	0.002	0.000004
0.034	0.008	0.000064
0.024	0.002	0.000004
0.036	0.010	0.000100
0.024	0.002	0.000004
0.024	0.002	0.000004

 $|x - \bar{x}|$ $\sum (x - \bar{x})^2$
 $\Sigma = 0.234$
 $\bar{x}_{3.8,24} = 0.026$
 $\Sigma = 0.000224$
 $S^2 = 0$
 $\sigma = 0.0005$
 $x_{-3.8,48}$ $|x - \bar{x}|$ $\sum (x - \bar{x})^2$

0.040	0.004	0.000016
0.056	0.012	0.000144
0.044	0	0
0.064	0.020	0.000400
0.056	0.012	0.000144
0.022	0.	0.000484
0.040	0.004	0.000016
0.040	0.004	0.000016
0.030	0.014	0.000196

 $\Sigma = 0.396$
 $\bar{x}_{-3.8,48} = 0.044$
 $\Sigma = 0.001416$
 $S^2 = 0.0002$
 $\sigma = 0.0125$

TABLE B-11

CYANIDE CONCENTRATIONS AND AMP HOURS USAGE
IN STANDARD LITHIUM CELLS DISCHARGED TO THE
2.40 AND 2.00 VOLT LEVELS

<u>CELL NUMBER</u>	<u>AMP HOURS</u>	<u>CYANIDE CONCENTRATION</u> (mg/l -24 Hrs)
<u>2.40 Volts</u>		
1	8.42	0.30
2	7.60	0.52
3	8.76	1.06
4	8.79	1.80
5	8.38	2.60
6	7.82	0.14
7	8.56	0.56
8	7.60	0.70
9	8.71	0.64
\bar{X}	8.29	0.92
S^2	0.21	0.61
σ	0.49	0.78
<u>2.00 Volts</u>		
1	9.71	4.00
2	9.28	8.80
3	9.44	4.40
4	9.98	4.00
5	9.56	6.80
6	9.52	8.80
7	9.72	4.00
8	9.17	6.40
9	9.08	3.20
\bar{X}	9.50	5.60
S^2	0.074	4.16
σ	0.29	2.16

TABLE B-12

CYANIDE CONCENTRATIONS AND AMP HOURS USAGE IN STANDARD LITHIUM CELLS DISCHARGED TO THE 1.70 AND 0.10 VOLT LEVELS

<u>CELL NUMBER</u>	<u>AMP HOURS</u>	<u>CYANIDE CONCENTRATION</u> (mg/l - 24 Hrs)
<u>1.7 Volts</u>		
1	9.55	1.60
2	9.97	3.75
3	9.24	6.40
4	9.95	10.20
5	9.97	2.65
6	9.36	4.00
7	9.40	4.25
8	9.24	5.20
9	9.31	1.60
\bar{X}	9.55	4.40
S^2	0.091	7.20
σ	0.32	2.68
<u>0.1 Volts</u>		
1	10.71	6.60
2	10.34	17.20
3	10.24	16.80
4	10.92	11.00
5	10.70	25.80
6	10.54	25.20
7	10.56	17.20
8	10.34	20.40
9	10.64	12.40
\bar{X}	10.55	16.90
S^2	0.042	40.20
σ	0.217	6.34

TABLE B-13

CYANIDE CONCENTRATIONS AND AMP HOURS USAGE IN STANDARD
LITHIUM CELLS DISCHARGED TO THE 1.70 AND 0.10 VOLT
LEVELS AND PLACED IN BUFFERED SOLUTIONS

<u>CELL NUMBER</u>	<u>AMP HOURS</u>	<u>CYANIDE CONCENTRATION</u> (mg/l - 24 Hrs)
<u>1.7 Volts</u>		
1	9.60	14.80
2	9.59	8.00
3	9.78	10.40
4	9.66	4.00
5	9.56*	7.60*
6	9.62	7.60
7	9.80	6.00
8	9.78	11.20
9	9.74	14.40
10	9.76	11.20
\bar{X}	9.69	9.73
S^2	0.008	11.84
σ	0.092	3.16
<u>0.1 Volts</u>		
1	9.56	2.00
2	9.38	14.00
3	9.41	7.20
4	9.50*	5.60*
5	9.74	5.20
6	9.52	6.00
7	9.39	9.60
8	9.51	13.20
9	9.64	8.00
10	9.32	4.80
\bar{X}	9.50	7.78
S^2	0.015	13.76
σ	0.128	3.93

*These data are not included in data base since cell discharged beyond target voltage.

TABLE B-14

CYANIDE CONCENTRATIONS AND AMP HOURS USAGE IN
STANDARD LITHIUM CELLS DISCHARGED TO NEGATIVE
VOLTAGE

<u>CELL NUMBER</u>	<u>FINAL VOLTAGE</u> (Volts)	<u>AMP HOURS</u>	<u>CYANIDE CONCENTRATION</u> (mg/l - 24 Hrs)
<u>Negative Voltage</u>			
1	-2.48	10.22	18.80
2	-4.42	10.24	12.80
3	-4.90	10.24	28.00
4	-3.62	10.24	22.80
5	-4.50	10.31	18.80
6	-4.10	10.31	19.20
7	-3.21	10.42	12.80
8	-3.42	10.24	25.60
9	-3.00	10.24	19.20
10	-4.28	10.24	17.60
\bar{X}	-3.88	10.27	19.56
S^2	0.53	0.003	21.49
σ	0.77	0.06	4.89

TABLE B-15

CYANIDE CONCENTRATIONS AND AMP HOURS USAGE IN
MODIFIED LITHIUM CELLS DISCHARGED TO 1.70 AND
NEGATIVE VOLTAGE LEVELS

CELL
NUMBER

AMP
HOURS

CYANIDE
CONCENTRATION

(mg/l - 24 Hrs)

1.70 Volts

1	6.88	0.024
2	6.76	0.044
3	7.52	0.038
4	6.41	0.038
5	6.88	0.030
6	7.42	0.016
7	7.68	0.036
8	7.80	0.032
9	7.60	0.030
10	7.54	0.028
\bar{X}	7.25	0.032
S^2	0.185	0.0001
σ	0.43	0.008

CELL
NUMBER

FINAL
VOLTAGE (Volts)

AMP
HOURS

CYANIDE
CONCENTRATION

(mg/l - 24 Hrs)

1	-3.8	8.44	0.024
2	-3.9	8.44	0.024
3	-3.9	8.44	0.020
4	-2.6	8.44	0.024
5	-4.0	8.44	0.034
6	-4.0	8.44	0.024
7	-4.3	8.44	0.036
8	-3.9	8.44	0.024
9	-4.2	8.44	0.024
\bar{X}	-3.84	8.44	0.026
S^2	0.216	0.00	0.000
σ	0.49	0.00	0.003

TABLE B-16

RESULTS OF LABORATORY ANALYSIS OF LEACHATE FROM DISCHARGED STANDARD
LITHIUM CELLS THROUGH A SANDY LOAM SOIL COLUMN

Date	Time	pH	Cond. (μ mhos)	Temp. (C°)	Sample Volume (ml)	Cyanide Conc. (mg/l)
1/27	1335	6.83	225	18.9	300	-
1/28	1410	5.90	220	18.7	470	-
1/29	1300	6.43	6,000	19.2	500	10.5
1/30	1319	6.39	12,050	18.9	250	27.0
2/1	1330	6.35	12,050	19.2	300	30.0
2/3	1407	6.34	10,300	18.9	200	37.8
2/4	1409	6.39	9,900	19.6	200	39.0
2/5	1136	6.39	6,900	18.8	320	34.0
2/7	1255	6.31	6,700	19.0	335	32.0
2/9	1300	6.80	5,500	18.6	200	27.0
2/11	1342	6.90	9,000	18.9	200	32.0
2/14	1301	6.83	10,600	19.3	200	-
2/15	1341	7.00	7,800	19.0	200	17.0
2/16	1342	7.31	3,150	19.3	250	4.0
2/17	1340	7.31	2,000	18.7	200	1.1
2/18	1353	7.21	1,310	19.9	210	0.70
2/19	1310	6.30	1,000	17.7	200	0.82
2/20	1145	7.28	870	19.6	210	-
2/22	1339	7.25	465	18.8	320	0.92

TABLE B-17

RESULTS OF LABORATORY ANALYSIS OF LEACHATE FROM LIVE STANDARD
LITHIUM CELLS THROUGH A SANDY LOAM SOIL COLUMN

Date	Time	pH	Cond. (μ mos)	Temp. ($^{\circ}$ C)	Sample Volume (ml)	Cyanide Conc. (mg/l)
1/24	1105	5.55	130	19.8	600	0.005
1/25	1005	5.63	125	22.0	430	0.005
1/26	1108	5.85	205	21.6	275	0.006
1/27	1330	5.83	3,210	20.7	500	0.042
1/28	1406	6.30	12,900	18.9	500	1.40
1/29	1300	11.82	22,000	19.1	500	1.20
1/30	1316	11.78	19,800	18.4	250	0.84
1/31	1230	11.83	17,600	19.1	250	0.86
2/2	1135	11.68	16,300	18.9	295	0.77
2/3	1405	11.60	14,300	19.2	200	0.49
2/4	1401	11.52	11,600	19.3	200	0.33
2/6	1253	11.45	9,000	18.7	335	0.21
2/8	0932	11.35	7,400	19.0	260	0.15
2/15	1335	11.26	4,150	18.6	240	0.11
2/17	1337	11.20	3,700	18.9	220	0.05
2/19	1309	11.00	3,050	20.1	230	0.04
2/20	1133	11.12	2,920	19.8	250	0.03
2/22	1341	11.00	1,890	19.6	300	<0.02

TABLE B-18
RESULTS OF LABORATORY ANALYSIS LEACHATE FROM SANDY
LOAM CONTROL COLUMN

Date	Time	pH	Cond. (μ mhos)	Temp. ($^{\circ}$ C)	Sample Volume (mL)	Cyanide Conc. (mg/1)
1/27	1340	6.09	260	19.0	550	0.006
1/28	1420	6.49	260	19.3	335	0.014
1/29	1310	6.54	430	18.7	350	0.050
1/30	1325	6.18	250	18.5	290	0.012
1/31	1235	6.70	250	19.1	250	0.016
2/1	1340	6.71	250	18.7	250	0.033
2/2	1138	6.70	250	18.6	250	0.14
2/3	1410	6.68	250	19.1	250	0.061
2/4	1410	6.68	210	18.1	250	0.074
2/5	1139	6.61	250	18.6	250	0.075
2/6	1259	6.75	260	18.7	250	0.050
2/7	1258	6.81	230	19.0	250	0.111
2/9	1300	6.90	180	18.7	230	0.012
2/11	1346	7.00	210	18.8	200	0.008
2/14	1305	7.05	200	18.6	300	0.024
2/16	1348	7.20	220	20.3	200	0.01
2/18	1356	6.60	205	20.1	220	0.007
2/28	1316	6.80	210	19.8	460	<0.005

TABLE B-19

RESULTS OF LABORATORY ANALYSIS OF LEACHATE FROM DISCHARGED
STANDARD LITHIUM CELLS THROUGH SILTY LOAM SOIL COLUMN

Date	Time	pH	Cond. (μ mhos)	Temp. ($^{\circ}$ C)	Sample Volume (ml)	Cyanide Conc. (mg/l)
4/25	1630	7.5	360	24.0	200*	<0.005
5/11	0915	7.6	375	20.0	260	<0.005
5/24	1435	7.7	1,300	25.0	235	0.010
6/6	0930	6.8	4,400	25.0	400	7.61
6/17	1315	5.4	18,000	25.0	210	36.8
7/5	1345	5.1	21,000	27.0	290	47.0
7/19	1300	4.5	10,000	29.5	200	70.0
8/3	1100	3.8	11,000	21.5	200	62.0
8/26	0900	2.7	5,000	25.0	270	51.0
9/21	1140	2.4	8,500	23.0	265	40.0
10/14	0830	2.4	11,000	18.0	220	32.0
11/1	0820	2.3	10,700	20.0	200	3.25

* A cumulative volume of 1410 mls of leachate had been collected previous to this sample.

TABLE B-20

RESULTS OF LABORATORY ANALYSIS OF LEACHATE FROM LIVE
STANDARD LITHI M CELLS THROUGH A SILTY LOAM SOIL COLUMN

Date	Time	pH	Ccnd. (μ mhos)	Temp. ($^{\circ}$ C)	Sample Volume (ml)	Cyanide Conc. (mg/l)
3/22	1310	8.00	415	20.0	200*	0.019
6/1	1355	7.60	700	25.0	170	<0.005
7/27	1605	7.4	370	26.0	200	<0.005
9/21	1130	7.8	270	23.0	200	<0.005
11/1	0830	6.6	460	19.0	190	<0.005

* A cumulative volume of 640 mls of leachate had been collected previous to this sample.

TABLE B-21

RESULTS OF LABORATORY ANALYSIS OF LEACHATE
THROUGH SILTY LOAM CONTROL COLUMN

Date	Time	pH	Cond. (μ mos)	Temp. ($^{\circ}$ C)	Sample Volume (ml)	Cyanide Conc. (mg/l)
3/14	1436	6.61	210	21.5	270	<0.005
3/22	1313	6.70	205	19.8	315	<0.005
4/6	0917	7.8	225	19.7	340	<0.005
4/18	1605	7.4	270	25.5	240	<0.005
4/28	1535	6.2	270	25.0	200	<0.005
5/13	1630	6.8	310	26.0	250	<0.005
5/24	1445	7.2	290	24.0	235	<0.005
6/1	1410	7.3	290	24.5	200	<0.005
6/15	1055	7.3	310	24.5	300	<0.005
6/27	1520	6.5	330	26.0	260	<0.005
7/11	1530	6.8	320	26.0	250	<0.005
7/22	1445	7.6	300	26.0	210	<0.005
8/3	1110	7.2	300	23.0	200	<0.005
8/11	1635	7.2	300	27.0	230	<0.005
8/26	0915	6.6	230	24.0	350	<0.005
9/7	1030	7.8	170	25.0	280	<0.005
9/21	1150	6.6	240	23.0	395	<0.005
10/3	1435	-	200	23.0	240	<0.005
10/14	0840	6.5	250	17.5	190	<0.005
11/1	0810	6.9	268	20	330	<0.005

TABLE B-22

RESULTS OF LABORATORY ANALYSIS OF LEACHATE FROM DISCHARGED STANDARD
LITHIUM CELLS THROUGH A SILTY CLAY SOIL COLUMN

Date	Time	pH	Cond. (μ mos)	Temp. ($^{\circ}$ C)	Sample Volume (ml)	Cyanide Conc. (mg/l)
2/3	1415	6.89	950	18.6	210	0.02
2/11	1351	7.83	670	19.6	215	0.005
2/18	1358	7.90	680	20.3	270	<0.005
2/28	1600	7.92	685	20.0	335	<0.005
3/8	1109	7.50	468	19.8	210	<0.005
3/22	1325	7.45	425	18.7	325	<0.005
4/6	0933	8.0	455	21.3	210	<0.005
4/25	1640	7.5	1,100	24.0	210	<0.005
5/16	1625	7.5	2,550	25.0	200	<0.005
6/6	0940	7.2	6,000	25.0	225	0.08
6/27	1600	6.8	15,000	25.0	200	23.2
7/19	1600	6.7	18,000	30.0	210	37.6
8/11	1600	6.7	19,000	29.0	180	88.4
9/7	1045	6.4	6,000	24.0	250	75.4
9/26	1630	-	7,000	27.0	240	52.1
10/18	1410	7.7	15,000	19.0	230	17.0
11/8	0815	8.2	14,000	20.0	245	7.50
12/19	1600	7.8	9,500	21.0	450	3.0

TABLE B-23

RESULTS OF LABORATORY ANALYSIS OF LEACHATE FROM LIVE STANDARD
LITHIUM CELLS THROUGH A SILTY CLAY SOIL COLUMN

Date	Time	pH	Cond. (μ mos)	Temp. ($^{\circ}$ C)	Sample Volume (ml)	Cyanide Conc. (mg/l)
1/26	1119	6.82	1,180	19.8	220	0.009
2/1	1352	6.99	1,190	19.1	230	0.011
2/8	0940	7.00	1,200	18.3	220	0.014
2/17	1346	7.40	910	20.1	270	0.008
2/22	1352	7.18	780	20.2	245	<0.005
3/8	1107	7.20	425	19.7	250	<0.005
3/22	1321	7.10	445	19.8	290	<0.005
4/6	0930	7.6	423	20.1	330	<0.005
4/28	1545	7.2	600	24.5	200	<0.005
5/27	0810	7.5	900	24.0	205	<0.005
6/27	1550	7.3	1,600	26.5	210	<0.005
8/3	1120	7.3	1,900	23.0	220	<0.005
9/21	1200	7.2	2,400	23.0	400	<0.005

TABLE B-24

RESULTS OF LABORATORY ANALYSIS OF LEACHATE THROUGH
A SILTY CLAY CONTROL COLUMN

Date	Time	pH	Cond. (μ mos)	Temp. ($^{\circ}$ C)	Sample Volume (ml)	Cyanide Conc. (mg/l)
1/26	1120	6.79	1,410	19.2	250	0.015
1/28	1426	6.79	1,200	18.7	310	0.016
1/30	1335	6.79	1,250	18.4	310	0.021
2/1	1358	6.69	1,180	18.7	310	0.025
2/3	1420	7.05	870	18.9	260	0.022
2/5	1141	6.95	820	17.2	250	0.028
2/7	1302	7.10	860	18.7	250	0.025
2/9	1300	7.5	700	18.3	250	0.004
2/11	1356	7.54	710	19.9	250	0.002
2/14	1307	7.60	705	18.7	375	<0.005
2/16	1342	6.98	780	19.2	250	0.008
2/18	1359	7.00	720	19.6	270	0.022
2/20	1151	7.12	700	19.4	275	0.014
2/22	1356	7.05	710	19.6	270	0.008
3/2	1322	7.00	715	20.2	290	<0.005
3/5	1544	7.10	705	19.2	350	<0.005
3/8	1108	7.05	610	20.1	400	<0.005
3/14	1442	7.10	630	20.6	350	<0.005
3/22	1328	7.13	615	20.1	475	<0.005
4/14	1035	7.1	600	23.5	750	<0.005
4/18	1615	7.8	460	23.5	425	<0.005
4/20	1510	7.2	460	26.0	375	<0.005
4/25	1650	7.4	430	23.0	250	<0.005
4/28	1600	7.1	440	24.5	275	<0.005
5/2	1020	7.2	430	25.0	350	<0.005
5/6	0850	7.5	430	25.8	350	<0.005

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